

10/804,747

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NEWS 7 MAR 03 MEDLINE file segment of TOXCENTER reloaded
NEWS 8 MAR 22 KOREAPAT now updated monthly; patent information enhanced
NEWS 9 MAR 22 Original IDE display format returns to REGISTRY/ZREGISTRY
NEWS 10 MAR 22 PATDPASPC - New patent database available
NEWS 11 MAR 22 REGISTRY/ZREGISTRY enhanced with experimental property tags
NEWS 12 APR 04 EPFULL enhanced with additional patent information and new
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NEWS 13 APR 04 EMBASE - Database reloaded and enhanced
NEWS 14 APR 18 New CAS Information Use Policies available online
NEWS 15 APR 25 Patent searching, including current-awareness alerts (SDIs),
based on application date in CA/Caplus and USPATFULL/USPAT2
may be affected by a change in filing date for U.S.
applications.
NEWS 16 APR 28 Improved searching of U.S. Patent Classifications for
U.S. patent records in CA/Caplus
NEWS 17 MAY 23 GBFULL enhanced with patent drawing images
NEWS 18 MAY 23 REGISTRY has been enhanced with source information from
CHEMCATS
NEWS 19 JUN 06 STN Patent Forums to be held in June 2005
NEWS 20 JUN 06 The Analysis Edition of STN Express with Discover!
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NEWS 21 JUN 13 RUSSIAPAT: New full-text patent database on STN
NEWS 22 JUN 13 FRFULL enhanced with patent drawing images

NEWS EXPRESS JUNE 13 CURRENT WINDOWS VERSION IS V8.0, CURRENT
MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP),
AND CURRENT DISCOVER FILE IS DATED 13 JUNE 2005

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FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005

=> fil reg

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005

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STRUCTURE FILE UPDATES: 14 JUN 2005 HIGHEST RN 852282-01-0

DICTIONARY FILE UPDATES: 14 JUN 2005 HIGHEST RN 852282-01-0

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TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

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*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
<http://www.cas.org/ONLINE/DBSS/registryss.html>

=> s formaldehyde/cn

L1 1 FORMALDEHYDE/CN

=> d l1

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
 RN 50-00-0 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN Formaldehyde (SCI, SCI) (CA INDEX NAME)
 OTHER NAMES:
 CN BIV
 CN F-ysn
 CN Fannoform
 CN Floguard 1015
 CN FM 282
 CN Fordor
 CN Formalin
 CN Formalith
 CN Formic aldehyde
 CN Formol
 CN Fyde
 CN Lysiform
 CN Methaldehyde
 CN Methanal
 CN Methyl aldehyde
 CN Methylene oxide
 CN Morbicide
 CN NSC 298885
 CN Oxomethane
 CN Oxymethylene
 CN Paraform
 CN Superlysoform
 FS 3D CONCORD
 DR 8005-38-7, 8006-07-3, 8013-13-6, 112068-71-0
 MF C H2 O
 CI COM
 LC STN Files: ADISNEWS, AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN*, BIOBUSINESS,
 BIOSIS, BIOTECHNO, CA, CABA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CBNS,
 CEN, CHEMCATS, CHEMINFORMX, CHEMLIST, CHEMSAFE, CIN, CSCHED, CSNS,
 DDFU, DETHERM*, DIOGENES, DIPPR*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2,
 ENCOMPAT, ENCOMPAT2, GMLIN*, HODOC*, HSDB*, IFICDB, IFIPAT, IFIUDB,
 IPA, MEDLINE, MRCK*, MSDS-OHS, NAPRALERT, NIOSHTIC, PDLCOM*, PIRA,
 PROMT, PS, RTECS*, SPECINFO, TOXCENTER, TULSA, ULIDAT, USAN, USPAT2,
 USPATFULL, VETU, VTB
 (*File contains numerically searchable property data)
 Other Sources: DSL**, EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)

H₂C=O

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

67660 REFERENCES IN FILE CA (1907 TO DATE)
 6465 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 67727 REFERENCES IN FILE CAPLUS (1907 TO DATE)
 19 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> fil caplus
COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
6.87	7.08

FULL ESTIMATED COST

FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
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FILE COVERS 1907 - 15 Jun 2005 VOL 142 ISS 25
FILE LAST UPDATED: 14 Jun 2005 (20050614/ED)

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This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s 50-00-0/rn
67727 50-00-0
6471 50-00-0D
L2 61794 50-00-0/RN
(50-00-0 (NOTL) 50-00-0D)

=> s N-methyl?
2806619 N
1652749 METHYL?
884815 ME
10009 MES
890941 ME
(ME OR MES)
2109049 METHYL?
(METHYL? OR ME)
L3 166261 N-METHYL?
(N(W) METHYL?)

=> s ?amine
L4 1415128 ?AMINE

=> s l2 and l3 and l4
L5 889 L2 AND L3 AND L4

=> s distill?
112316 DISTILL?
160014 DISTD
1 DISTDS
160014 DISTD

```

                (DISTD OR DISTDS)
      24603 DISTG
    171283 DISTN
      1746 DISTNS
    172012 DISTN
          (DISTN OR DISTNS)
L6      362618 DISTILL?
          (DISTILL? OR DISTD OR DISTG OR DISTN)

=> s 15 and 16
L7      47 L5 AND L6

=> d 17 1-47 abs ibib
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L7 ANSWER 1 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Formaldehyde (FA), an occupational and environmental toxicant used extensively in the manufacturing of many household and personal use products, is known to induce squamous cell carcinomas in the nasal turbinates of rats and mice and squamous metaplasia in monkey noses. Tissue responses to FA include a dose dependent epithelial degeneration, respiratory cell hypertrophy, and squamous metaplasia. The primary target for FA-induced toxicity in both rodents and monkeys is the respiratory nasal epithelium. FA increases nasal epithelial cell proliferation and DNA-protein crosslinks (DPX) that are associated with subsequent nasal cancer development. To address the acute effects of FA exposure that might contribute to known pathol. changes, cDNA gene expression anal. was used. Two groups of male F344 rats received either 40 ul of distilled water or FA (400 mg) instilled into each nostril. Twenty-four hours following treatment, nasal epithelium was recovered from which total RNA was used to generate cDNA probes. Significance anal. of microarrays (SAM) hybridization data using Clontech Rat Atlas 1.2 arrays revealed that 24 of the 1185 genes queried were significantly up-regulated and 22 genes were significantly downregulated. Results for ten of the differentially expressed genes were confirmed by quant. real time RT-PCR. The identified genes with FA-induced change in expression belong to the functional gene categories xenobiotic metabolism, cell cycle, apoptosis, and DNA repair. These data suggest that multiple pathways are dysregulated by FA exposure, including those involved in DNA synthesis/repair and regulation of cell proliferation. Differential gene expression profiles may provide clues that could be used to define mechanisms involved in FA-induced nasal cancer.

ACCESSION NUMBER: 2003:250610 CAPLUS
 DOCUMENT NUMBER: 139:192642
 TITLE: Formaldehyde-induced gene expression in F344 rat nasal respiratory epithelium
 AUTHOR(S): Hester, Susan D.; Benavides, Gina B.; Yoon, Lawrence; Morgan, Kevin T.; Zou, Fei; Barry, William; Wolf, Douglas C.
 CORPORATE SOURCE: US Environmental Protection Agency, Research Triangle Park, NC, USA
 SOURCE: Toxicology (2003), 187(1), 13-24
 CODEN: TXXYAC; ISSN: 0300-483X
 PUBLISHER: Elsevier Science Ireland Ltd.
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 REFERENCE COUNT: 31 THERE ARE 31 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L7 ANSWER 2 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB A process for preparing trimethylol compds. (e.g., trimethylolpropane) and formic acid by the reaction of formaldehyde and aldehydes RCH₂CHO [R = (un)substituted alkyl, (un)substituted cycloalkyl, (un)substituted aryl, (un)substituted aralkyl; e.g., butyraldehyde] in the presence of a nitrogen base (e.g., triethylamine) with distillation of the resulting reaction mixture in the presence of an auxiliary (e.g., N-methylpyrrolidone) is described. A process flow diagram is presented.

ACCESSION NUMBER: 2002:466749 CAPLUS
 DOCUMENT NUMBER: 137:33975
 TITLE: Process for preparing trimethylol compounds and formic acid from aldehydes and formaldehyde
 INVENTOR(S): Dobert, Frank; Wagner, Paul; Klausener, Alexander; Eymann, Wolfgang; Feller, Rolf
 PATENT ASSIGNEE(S): Germany
 SOURCE: U.S. Pat. Appl., 8 pp.
 CODEN: USXXCO
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2002077502	A1	20020620	US 2001-17816	20011213
US 6441254	B2	20020827		
DE 10063937	A1	20020718	DE 2000-10063937	20001220
EP 1216979	A1	20020626	EP 2001-128486	20011207
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
JP 2002193854	A2	20020710	JP 2001-380156	20011213
CN 1359886	A	20020724	CN 2001-143351	20011230
PRIORITY APPLN. INFO.:			DE 2000-10063937	A 20001220
OTHER SOURCE(S):			MARPAT 137:33975	

L7 ANSWER 3 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Heteroatom-rich hydrocarbon oils (especially shale oils) are processed by solvent extraction with a polar solvent mixture containing a major amount of a polar solvent (with dipole moment >1 D), and a minor amount of water (as antisolvent), with, optionally, a minor amount of a C5-7-hydrocarbon (n-alkane, isoalkane, and cycloalkane), to yield a heteroatom-depleted raffinate and a heteroatom-rich extract. The proportions of the polar solvent, water, and hydrocarbon are selected such that the coefficient of separation is >50%.

Suitable polar solvents are selected from formaldehyde, formic acid, MeOH, acetaldehyde, HOAc, EtOH, propanol, isopropanol, furfural, phenol, sulfolane, N-methyl-2-pyrrolidone, and C8-10-carboxylic acids, aldehydes, ketones, ethers, esters, and amines. Addnl. refining options were described for further and sep. processing of both the raffinate and extract fractions (following distillation for removal of solvent, with appropriate recirculation back to the extraction step). The raffinate can be further processed to provide a high-quality synthetic crude petroleum for further refining. The heteroatom-rich extract can be used for the manufacture of a number of specialty chems., such as lubricant and fuel additives, biocides and pesticides, asphalt binders, solvents, diluting and solubilizing agents, etc.

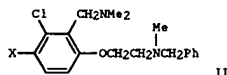
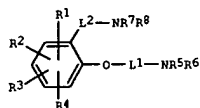
ACCESSION NUMBER: 2000:842094 CAPLUS
 DOCUMENT NUMBER: 134:31135
 TITLE: Extraction with polar solvent-water antisolvent mixture for removal of heteroatomic compounds from shale oils
 INVENTOR(S): Bunger, James W.; Cogswell, Donald E.
 PATENT ASSIGNEE(S): James W. Bunger and Associates, Inc., USA
 SOURCE: PCT Int. Appl., 69 pp.
 CODEN: PIXX02
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2000071494	A1	20001130	WO 2000-US14128	20000523
V: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, BG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
EE 200100622	A	20030217	EE 2001-622	20000523
US 6875341	B1	20050405	US 2001-979702	20011126
PRIORITY APPLN. INFO.:			US 1999-135611P	P 19990524
			WO 2000-US14128	W 20000523
REFERENCE COUNT: 12				
				THERE ARE 12 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L7 ANSWER 4 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The oxazolidine derivs. (as corrosion inhibitors) are produced by condensation of N-methylethanolamine with aliphatic aldehydes in equi-mol. amts. in the presence of a neutral organic solvent. Preferably, the resulting products are purified by vacuum distillation. Optionally, the products are dissolved in an oil base.

ACCESSION NUMBER: 1998:360777 CAPLUS
 DOCUMENT NUMBER: 128:324754
 TITLE: Volatile corrosion inhibitors for steels
 INVENTOR(S): Marczak, Ryszard; Maciag, Artur; Prot, Tomasz; Wilczek, Maria
 PATENT ASSIGNEE(S): Politechnika Radomska Im Kazimierza Pulaskiego, Pol.
 SOURCE: Pol., 4 pp.
 CODEN: POXXA7
 DOCUMENT TYPE: Patent
 LANGUAGE: Polish
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PL 173103	B1	19980130	PL 1994-301910	19940114
PRIORITY APPLN. INFO.:			PL 1994-301910	19940114



AB The title compds. [I; R1 - R4 = H, halo, halo, halogenated alkyl, halogenated alkoxy, alkyl, alkoxy, cyano, a carbamoyl group of formula CONR_aR_b (wherein R_a, R_b = alkyl), alkoxy carbonyl group; or R1 and R2 together with the Ph ring represent an (un)substituted naphthalene ring; L1 = C2-6 alkylene optionally substituted by one or more C1-4 alkyl groups; R5 = H, alkyl; R6 = H, alkyl, (un)substituted phenylalkyl; or R5 and R6 together with the nitrogen atom to which they are attached represent a saturated 3-7 membered heterocyclic ring; L2 = C1-6 alkylene

chain optionally substituted by one or more C1-4 alkyl groups; R7, R8 = H, alkyl; or R7 and R8 together with the nitrogen atom to which they are attached represent a saturated 3-7 membered heterocyclic ring] or pharmaceutically acceptable salts thereof which are antiinflammatory and/or antiallergic agents and/or immunomodulators and useful in treating rheumatic diseases and/or neuropathic damage, are prepared Thus, 5.25 mL N-benzyl-N-methylethanolamine, 8.48 g Ph3P, and 5.09 mL di-Et azodicarboxylate were added to a solution of 6.0 g 3-chloro-2-(dimethylaminomethyl)phenol in THF and the resulting mixture was stirred at ambient temperature for 24 h to give, after vacuum distillation and treatment with ethereal HCl, a benzylamine derivative (II.2HCl; X = H). This compound and II.2HCl (X = Cl) in vitro inhibited the arachidonic acid release from zymosan-stimulated macrophages with IC50 of 15 and 8 µM, resp., and in vivo at 100 mg/kg p.o. inhibited 70% the carrageenan-induced paw edema in rats.

ACCESSION NUMBER: 1995:994305 CAPLUS
DOCUMENT NUMBER: 124:55553
TITLE: Preparation of 2-(aminoalkoxy)phenylalkylamines with antiinflammatory activity
INVENTOR(S): Rafferty, Paul; Tometzki, Gerald Bernard
PATENT ASSIGNER(S): Boots Co. PLC, UK
SOURCE: PCT Int. Appl., 100 pp.
CODEN: PIXKX2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9523127	A1	19950831	WO 1995-EP626	19950220
W: AM, AT, AU, BE, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT,				

AB Disclosed is a one-step method for preparing N-alkylpiperazines which eliminates the initial preparation and isolation of piperazine which comprises reacting a carbonyl compound R''COR' where R'' and R' = an alkyl group or H, and an amine H2NCH2CH2NHCOR' where R''' is OH or NH2 in the presence of hydrogen over a metallic hydrogenation catalyst consisting essentially of nickel, copper and chromium. Thus, e.g., reaction of aminoethylethanolamine (208 g) with isobutyraldehyde (144 g) followed by hydrogenation/cyclization over nickel-copper-chromium catalyst afforded the iso-Bu derivative of aminoethylethanolamine as the main product; however, the ratio of isobutylpiperazine to piperazine was about 8:1. In comparison, the reaction of piperazine with isobutyraldehyde followed by hydrogenation over nickel-copper-chromium catalyst afforded a material that contained 21% piperazine and 30% N-isobutylpiperazine;

separation of piperazine from the isobutylpiperazine was difficult (even though the isobutylpiperazine boiled at 182°) because piperazine deposited throughout the distillation train.

ACCESSION NUMBER: 1995:616516 CAPLUS
DOCUMENT NUMBER: 123:55921
TITLE: One-step preparation of N-alkylpiperazines which eliminates the initial preparation and isolation of piperazine
INVENTOR(S): Speranza, George P.; Templeton, James H.
PATENT ASSIGNER(S): Huntsman Corporation, USA
SOURCE: U.S., 5 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5414087	A	19950509	US 1993-87093	19930707
PRIORITY APPL. INFO.:			US 1993-87093	19930707
OTHER SOURCE(S):			CASREACT 123:55921; MARPAT 123:55921	

UA, US
RW: KE, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG
AU 9517586 A1 19950911 AU 1995-17586 19950220
EP 750607 A1 19970102 EP 1995-910506 19950220
EP 750607 B1 19990506
R: DE, FR, GB, IT
JP 09509422 T2 19970922 JP 1995-522119 19950220
ZA 9501420 A 19950825 ZA 1995-1420 19950221
US 5736568 A 19980407 US 1996-687584 19961125
PRIORITY APPL. INFO.: GB 1994-3639 A 19940225
WO 1995-EP626 W 19950220
OTHER SOURCE(S): MARPAT 124:55553

AB In a process for production of an aromatic azomethine by reaction of an aniline with formaldehyde, formaldehyde is provided in the form of a product produced by contacting paraformaldehyde with from about 0.25 to about 3 mol equivalent of an aliphatic alc. having from 1 to 4 carbon atoms in the presence of a catalytic amount of a base. The azomethine may then be used to produce a haloacetanilide. Thus, e.g., one reactor was charged with 3.0 mol paraformaldehyde, 3.0 mol ethanol, 0.01 mol triethylamine, 1.0 mol xylene and 0.5 mol water, heated to 85-90° and agitated until the solution was clear; this solution was added to a reactor containing 1 mol of 2-methyl-6-ethylaniline and 2 mol of xylene at about 90°; the reaction was allowed to proceed with azeotropic distillation of water at atmospheric pressure at 95-126°; addition of chloroacetyl chloride afforded 96-97% of the N-chloromethyl-α-chloroacetanilide derivative

ACCESSION NUMBER: 1995:603984 CAPLUS
DOCUMENT NUMBER: 123:111656
TITLE: Process for producing aromatic azomethines by reaction of an aniline with formaldehyde provided in the form of a formaldehyde-alcohol complex
INVENTOR(S): Rodriguez, Gilbert
PATENT ASSIGNER(S): Imperial Chemical Industries PLC, UK
SOURCE: U.S., 7 pp. Cont.-in-part of U.S. Ser. No. 680,468, abandoned.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5399759	A	19950321	US 1992-872775	19920422
HU 65592	A2	19940728	HU 1993-2620	19920320
HU 219568	B	20010528		
AT 154000	E	19970615	AT 1992-910655	19920320
ES 2102503	T3	19970801	ES 1992-910655	19920320
ZA 9202455	A	19930329	ZA 1992-2455	19920403
IL 101484	A1	19970415	IL 1992-101484	19920403
PRIORITY APPL. INFO.:			US 1991-680468	B2 19910404
OTHER SOURCE(S):			CASREACT 123:111656; MARPAT 123:111656	

L7 ANSWER 8 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
AB The title polymers, useful in moldings, films, and fibers (no data), are prepared by the reaction of polymers containing the ethers $\text{CH}_2\text{C}(\text{X})\text{CH}_2\text{CH}_2\text{C}(\text{Y})\text{CH}_2$ (X, Y = CO₂H, carboalkoxy, acyl, amido, or CN group) 1-99, (meth)acrylic acid or their (cyclo)alkyl esters 99-1, and comonomers 0-99% with primary amines of specified structure. Peroxy ester-initiated polymerization of 60 g di-Me 2,2'-(oxydimethylene)diacrylate (prepared from Me acrylate and paraformaldehyde in the presence of triethylenediamine) with 140 g MMA in THF at 65° gave 190 g copolymer, which was heated (10 g) with 10 g cyclohexylamine in N-methylpyrrolidone for 6 h with distillation of MeOH to give a polymer with N content 5.1% and glass temperature 235°.

ACCESSION NUMBER: 1994:192636 CAPLUS
DOCUMENT NUMBER: 120:192636
TITLE: Polymethacrylamides with high heat distortion resistance
INVENTOR(S): Bessecke, Siegmund; Deckers, Andreas; Lauke, Harald
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: Eur. Pat. Appl., 15 pp.
CODEN: EPXOKDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 561230	A2	19930922	EP 1993-103460	19930304
EP 561230	A3	19931027		
EP 561230	B1	19960529		
R: BE, CH, DE, FR, GB, IT, LI, NL				
DE 4208994	A1	19930923	DE 1992-4208994	19920320
US 5338805	A	19940816	US 1993-31907	19930316
			DE 1992-4208994	A 19920320

PRIORITY APPLN. INFO.:
OTHER SOURCE(S):

L7 ANSWER 9 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
GI



AB Title amines I (R = cyclohexyl, C1-6 linear or branched alkyl group) prepared by methylation with H₂CO are purified by a distillation process involving: (i) preliminary distillation of MeOH, H₂CO, and a portion of H₂O; (ii) addition of 5-20-fold portion of C8-12 arylalkanes and/or cycloalkylalkanes (based on combined 5-15 mol% water content + HCO₂H content (as formate salt)); (iii) continuous distillation of the resultant mixture (with inert gas bubbling and/or reduced pressure, as necessary) for 4-10 h with return of arylalkanes and/or cycloalkylalkanes to the distillation apparatus. Thus, the reaction mixture resulting from methylation of cyclohexylamine with H₂CO was submitted to preliminary distillation for MeOH and partial H₂O removal, resulting in the composition: 1 (R = Me) (90.2 mol%), other amines (0.4 mol%), H₂O (8 mol%), HCO₂H (1.4 mol%). To 1000 g of this mixture was added 800 g xylene mixture, and the resulting solution was distilled for 8 h with Ar bubbling (15 dm³) for 1 h. H₂O and HCO₂H were removed as a sep. phase, and the xylene mixture was returned to the distillation apparatus I (R = Me)

was obtained H₂O- and HCO₂H-free, in 99.7 mol% purity, by addnl. distn

ACCESSION NUMBER: 1993:233533 CAPLUS
DOCUMENT NUMBER: 118:233533
TITLE: Process for purification of tertiary cyclohexylamines obtained by methylation with formaldehyde
INVENTOR(S): Palkovics, Istvan; Magi, Gabor, Mrs.; Torkos, Laszlo; Aranyi, Peter; Gemes, Istvan; Novotnik, Katalin
PATENT ASSIGNEE(S): Nitroil Vegyipari Termelo-Fejleszto Rt., Hung.
SOURCE: Hung. Teljes, 9 pp.
CODEN: HUXKBU
DOCUMENT TYPE: Patent
LANGUAGE: Hungarian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
HU 61265	A2	19921228	HU 1991-439	19910211
HU 208667	B	19931228		

PRIORITY APPLN. INFO.: HU 1991-439 19910211
OTHER SOURCE(S): MARPAT 118:233533

L7 ANSWER 10 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
AB The hazardous materials regulations under the Federal Hazardous Materials Transportation Act are revised based on the United Nations recommendations on the transport of dangerous goods. The regulations cover the classification of materials, packaging requirements, and package marking, labeling, and shipping documentation, as well as transportation modes and handling, and incident reporting. Performance-oriented stds. are adopted for packaging for bulk and nonbulk transportation, and SI units of measurement generally replace US customary units. Hazardous material descriptions and proper shipping names are tabulated together with hazard class, identification nos., packing group, label required, special provisions, packaging authorizations, quantity limitations, and vessel stowage requirements.

ACCESSION NUMBER: 1992:135528 CAPLUS
DOCUMENT NUMBER: 116:135528
TITLE: Performance-oriented packaging standards; changes to classification, hazard communication, packaging and handling requirements based on UN standards and agency initiative
CORPORATE SOURCE: United States Dept. of Transportation, Washington, DC, 20590-0001, USA
SOURCE: Federal Register (1990), 55(246), 52402-729, 21 Dec 1990
CODEN: FERFAC; ISSN: 0097-6326
DOCUMENT TYPE: Journal
LANGUAGE: English

L7 ANSWER 11 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
AB The continuous preparation of N,N-dimethylamines by the reaction of aldehydes with Me₂NH and hydrogen under pressure at high temperature in the presence of Ni, Co, Cu, Mn, Fe, Rh, Pd and/or Pt-containing hydrogenation catalysts is claimed. After remaining starting material (Me₂NH) and hydrogen are removed, 0.1-25% by weight HCHO or HCHO-forming substance are added and the mixture is distilled. This process permits nearly complete removal of secondary N-methylamines which are formed as by products. A reactor containing 300 mL catalyst RCH Ni52/35 (tablets; Ni catalyst on kieselguhr) was filled with Me₂NBu and then charged with PrCHO (65 mL) and Me₂NH (200 mL) at 105-110° and 8 MPa and hydrogen was charged at 34 L/hr remaining hydrogen and Me₂NH were removed and during the subsequent distillation 37% aqueous HCHO (apprx. 3% with respect to Me₂NBu) was fed into the crude product mixture at the bottom of the column. The distillate contained 99.65% by weight Me₂NBu and 0.02% by weight MeNH₂. Omission of feed of aqueous HCHO gave a distillate containing 98.09% by weight Me₂NBu and 1.22% by weight MeNH₂.

ACCESSION NUMBER: 1991:535511 CAPLUS
DOCUMENT NUMBER: 115:135511
TITLE: Process for the preparation of N,N-dimethylamines
INVENTOR(S): Kampmann, Detlef; Kniep, Claus; Lukas, Rainer
PATENT ASSIGNEE(S): Hoechst A.-G., Germany
SOURCE: Ger. Offen., 6 pp.
CODEN: GWXKXK
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 3942793	A1	19910627	DE 1989-3942793	19891223
EP 435072	A2	19910703	EP 1990-123912	19901212
EP 435072	A3	19920304		
EP 435072	B1	19940427		
R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE				
AT 104950	E	19940515	AT 1990-123912	19901212
ES 2055855	T3	19940901	ES 1990-123912	19901212
CA 2032362	AA	19910624	CA 1990-2032362	19901214
CA 2032362	C	20010327		
JP 06219993	A2	19940809	JP 1990-402867	19901217
JP 07072159	B4	19950802		
AU 9068373	A1	19910627	AU 1990-68373	19901221
AU 634807	B2	19930211		

PRIORITY APPLN. INFO.: DE 1989-3942793 A 19891223
EP 1990-123912 A 19901212



AB The title compds (I; A = C2-10 1,2- or 1,3-alkylene) were prepared by **S-methylation** of the parent cyclic urea using H₂CO and excess HCO₂H (the latter being removed by thermal decomposition in the presence of a tertiary amine and a Cu salt). Thus, a mixture of 1,3-propyleneurea 4 mol, HCO₂H 20 mol, 50% aqueous H₂CO 9-6 mol, Et₃N 40 mol, and CuCl 40 mol was refluxed 16 h followed by distillation of volatiles. Decomposition of HCO₂H began at 150° and was complete after 4-6 h. Final distillation of the mixt at 23 mbar and 106-108° gave 80% I [A = (CH₂)₃].

ACCESSION NUMBER: 1990:440719 CAPLUS
DOCUMENT NUMBER: 113:40719
TITLE: Preparation of cyclic N,N'-dimethylureas by methylation with formic acid and formaldehyde
INVENTOR(S): Betz, Rainer; Hahn, Erwin; Fikentscher, Rolf
PATENT ASSIGNEE(S): BASF A.-G., Germany
SOURCE: Eur. Pat. Appl., 6 pp.
CODEN: EPXKDW
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 356973	A1	19900307	EP 1989-115871	19890829
EP 356973	B1	19921111		
R: DE, FR, GB, IT				
DE 3829848	A1	19900315	DE 1988-3829848	19880902
US 4970321	A	19901113	US 1989-397878	19890823
JP 02115171	A2	19900427	JP 1989-217641	19890825
PRIORITY APPLN. INFO.:			DE 1988-3829848	A 19880902
OTHER SOURCE(S):			CASREACT 113:40719; MARPAT 113:40719	

L7 ANSWER 14 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB Wastewaters from thiazone manufacturing are acidified to pH 0.3-0.5 with H₂SO₄ or HCl to hydrolyze methylamine **S-methyldithiocarbamate**; the CS₂ formed is adsorbed on an activated C; HCHO is oxidized to HCOOH with air over a bed of pyrolusite; and the residual volatile organic compds. are removed by distillation

ACCESSION NUMBER: 1987:483309 CAPLUS
DOCUMENT NUMBER: 107:83309
TITLE: Treatment of wastewater from thiazone manufacture
AUTHOR(S): Marchenko, V. M.; Taran, P. N.
CORPORATE SOURCE: Inst. Kolloidn. Khim. Khim. Vody im. Dumanakogo, Kiev, USSR
SOURCE: Khimiya i Tekhnologiya Vody (1987), 9(3), 250-2
CODEN: KIVODL; ISSN: 0204-3556
DOCUMENT TYPE: Journal
LANGUAGE: Russian
OTHER SOURCE(S): CASREACT 107:83309

L7 ANSWER 13 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB **S-Me** tertiary amines are prepared by continuous treatment of HCHO with nitriles in the presence of hydrogenation catalysts at 80-180° under 3-50 kg/cm² gage H. Laurotrile (I) was autoclaved with Raney Ni at 140° under 10 kg/cm² gage H while adding an aqueous HCHO for 6 h and the reaction mixture was kept for 0.5 h, subsequently the reaction product was distilled to give 92.4% Me(CH₂)₁₁NMe₂, vs. 70.0% for a control by a two-step reaction comprising (1) hydrogenation of I at 120° under 20 kg/cm² gage H for 6 h and (2) purification of the resulting laurylamine and **S-methylation** under the same conditions.

ACCESSION NUMBER: 1989:406917 CAPLUS
DOCUMENT NUMBER: 111:6917
TITLE: Preparation of **S-methyl** tertiary amines from nitriles and formaldehyde
INVENTOR(S): Yokota, Yukinaga; Matsutani, Kazuto; Okabe, Kazuhiko
PATENT ASSIGNEE(S): Kao Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKOXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63287752	A2	19881124	JP 1987-120949	19870518
PRIORITY APPLN. INFO.:			JP 1987-120949	19870518

L7 ANSWER 15 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
AB A simple, rapid a.c. polarographic method for the determination of free and bound HCHO [50-00-0] in 0.1 N LiOH can be used to optimize methods for the production of HCH products, to follow the etherification of **S-methylol** compds. with alcs., and to analyze textiles finished with formaldehyde products. Free HCHO is determined at pH 9.2 since no dissociation of methylol groups occurs in this region; NCH₂OH, NCH₂OCH₂OH, and OCH₂OH are hydrolyzed in LiOH which also serves as the base electrolyte; NCH₂OMe, NCH₂OCH₂Me, and NCH₂OCH₂OMe were hydrolyzed by strong acids, the HCHO when free is distilled, and the distillate is analyzed polarog. When the substance to be analyzed produces interfering waves, as is the case with hexamethylolmelamine (I) [3089-11-0], the mercurimetric cyanide method is used to determine free HCHO.

Polarograms are given for I, N,N'-dimethylol-1,3-propyleneurea [3270-74-4], (MeO)2P(O)CH₂CH₂CONHCH₂OH [20120-33-6], and Movin DC [53200-17-2].

ACCESSION NUMBER: 1975:580860 CAPLUS
DOCUMENT NUMBER: 83:180860
TITLE: Determination of free and bound formaldehyde in textile auxiliary agents by alternating current polarography
AUTHOR(S): Linhart, Karl
CORPORATE SOURCE: Leverkusen, Fed. Rep. Ger.
SOURCE: Melliland Textilberichte International (1975), 56(3), 240-5
CODEN: MTXIAW; ISSN: 0375-9350
DOCUMENT TYPE: Journal
LANGUAGE: German

L7 ANSWER 16 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Carbamoyloxyalkyl esters of sulfoalkyl, carbamylalkyl, cyanoalkyl, or phosphonoalkyl phosphonates or phosphonites are fire retardants for textiles. Thus, addition over 30 min of 849 g ethylene carbonate [96-49-1] to 722 g 25%NH3 at 20-40.deg., stirring 3 hr at 40.deg. and 2 hr at 125-30.deg./10-25 mm, adding 1150 g diethyl phosphite [762-04-9] and 8 g NaOMe, heating 16 hr at 50.deg./5-20 mm with addition of 5 g NaOMe every 2

hr and distillation of EtOH, adding 440 g acrylonitrile [107-13-1] and 30-40g of 33% NaOMe over 45 min, and stirring 30 min at pH 7-9 gives 2080 g crude 2-(carbamoyloxy)ethyl ethyl (2-cyanoethyl)phosphonate (I) [52870-25-4]. Addition of 1 over 10 min to 740 g 37% HCHO (50-00-0) and .sim.10 g 33% NaOH and stirring 1 hr at 40-50.deg. and pH 9-10 gives 2900 g aqueous N-methylol derivative (II) [52870-36-7] of I.
 II Cotton fabric (320 g/m2) is padded to 75% uptake with a solution containing

350, hexamethylmelamine pentamethyl ether 40, and NH4Cl 4 g/l., dried to 6% residual moisture at 120.deg., and cured 4 min at 170.deg. to give a product which remains fire resistant (DIN 53 906) after 15 launderings.

ACCESSION NUMBER: 1974:554487 CAPLUS
 DOCUMENT NUMBER: 81:154487
 TITLE: Phosphorus compounds containing carbamate groups and their use as flame-protective additives
 INVENTOR(S): Diersch, Walter; Linke, Fritz; Beermann, Claus; Nischwitz, Ehrenfried
 PATENT ASSIGNEE(S): Farbwerke Hoechst A.-G.
 SOURCE: Ger. Offen., 42 pp.
 CODEN: GWOKRX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2249321	A1	19740502	DE 1972-2249321	19721007
DE 2249321	B2	19751030		
DE 2249321	C3	19760610		
CH 7314160	A4	19750415	CH 1973-14160	19731004
CH 567145	B	19750930		
CH 565810	A	19750829	CH 1975-2118	19731004
JP 49070951	A2	19740709	JP 1973-111603	19731005
US 3876601	A	19750408	US 1973-404096	19731005
AT 7308508	A	19750615	AT 1973-8508	19731005
AT 328409	B	19760325		
IT 995655	A	19751120	IT 1973-29825	19731005
GB 1429545	A	19760324	GB 1973-46598	19731005
CA 1000276	A1	19761123	CA 1973-182767	19731005
BE 805772	A1	19740408	BE 1973-136429	19731005
FR 2202100	A1	19740503	FR 1973-35832	19731008
PRIORITY APPLN. INFO.:			DE 1972-2249321	A 19721007

L7 ANSWER 17 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Compns. were prepared, which are useful in the treatment of leather, paper, glass, plastic, rubber, wood, and textiles, from water soluble or water dispersible salts of polyurethane resins, surfactants, epoxides, pigments, and solvents. The polyurethane resins were obtained by reacting an isocyanate terminated prepolymer with a OH containing N compound which is

the Mannich condensation product of a phenol, an aldehyde, and an alkanolamine. Thus, a OH-containing N compound was prepared as follows: a mixture of 315 g. (HOCH2CH2)2NH and 60 g. MeOH was cooled to 10°C., 244.5 g. 37% HCHO was added with stirring over 60 min., a mixture of 282 g. PhOH and 25 g. MeOH was added over 15 min. at 18-22°C., the mixture was stirred for 1 hr. at 18-22°C., heated to 65°C., stirred for 2 hrs. at 65°C., and the mixture was subjected to vacuum distillation to a pot temperature of 100°C. for 15 min. An isocyanate-terminated prepolymer was prepared as follows: 812 g. polyethylene glycol 1540 was added in 30 min. with agitation to 189 g. tolylene diisocyanate under N while maintaining the reaction temperature at 45-55°C. and the mixture was heated for 1 hr. at 80-5°C. To 500 g. melted prepolymer was added 105.5 g. of the OH containing N compound, the mixture was heated 90 min. at 90-5°C., cooled to 70°C., and a solution of 30 g. HOAc in 635.5 g. H2O was added to give a treating agent composition (I). A chrome tanned shaved side leather was put in a drum, 100 weight % water was added, the leather was washed at 100°F., drained, floated with 50 weight % water, heated to 100°F., 4% I was added, the mixture was agitated 1 hr., a solution at 100°F. containing 5% of a condensation product of urea, HCHO, and sulfonated cresol and 50% water based on the weight of the leather was added to the leather, the mixture was agitated 1 hr., drained, the leather washed 10 min. at 125°F. with water, drained, and fat-liquored for 45 min. at 125°F. with 5% sulfated vegetable and animal oils. The leather was pulled, horsed, and dried; the leather showed a tight grained effect and excellent temper. Other alkanolamines used in the preparation of the OH containing N compound

were monoethanolamine, N-methylmonoethanolamine, N-ethylmonoethanolamine, and N-benzyl-diethanolamine. Other prepolymers used were prepared from polypropylene glycol and tolylene diisocyanate. Other phenols used in the preparation of the OH containing N compound were nonylphenol and bisphenol A.
 4,4'-dihydroxydiphenylmethane was also claimed. The treating agent compns. were also used as pigment binders on fiber glass fabrics and glass fabrics were also coated with the treating compns. and then dyed. The treating agents also decreased the capacity of Dacron fabrics to retain electrostatic charges and improved the abrasion resistance of cotton fabrics. The treating agent was also used to bond glass fibers to a resorcinol-hCHO latex coating and as a tie bond coating for glass fiber roving.

ACCESSION NUMBER: 1969:482777 CAPLUS
 DOCUMENT NUMBER: 71:82777
 TITLE: Urethane composition
 INVENTOR(S): Sellet, Lucien
 PATENT ASSIGNEE(S): Diamond Alkali Co.
 SOURCE: U.S., 29 pp.
 CODEN: USXOAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

L7 ANSWER 17 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3462237	A	19690819	US 1965-475600	19650728
PRIORITY APPLN. INFO.:			US 1965-475600	A 19650728

L7 ANSWER 18 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Condensation products of an aromatic amine with an aliphatic or aromatic aldehyde are cast, brushed, or sprayed as solution or dispersion on an elec. conductive support to obtain transparent photoconductive layers which are charged, exposed, and developed with a toner powder fusing at 110-125°, as are conventional materials. Impregnation of a paper base to inhibit penetration by the solution is unnecessary. The unexposed coatings are removable by dilute acids in the preparation of printing plates.

Dyes can be added as optical sensitizers and electron acceptors with a mol. weight between 100 and 1000 and an absorption maximum in the uv range as activators. N-Ethylaniline and HCHO are condensed by a 2-stage process. In the first, N,N'-diethyl-N,N'-diphenylmethylenediamine, m. 79°, is produced by stirring for 3 days at room temperature a mixture of N-ethylaniline 726 parts by weight, 40% HCHO 225 parts by weight, and 2N NaOH 3 parts by volume. The filtered reaction product 245 parts by weight, HCHO 90 parts by volume, and HCl 240 parts by volume are heated 6 hrs. on a steam bath, and the condensate is isolated as amber-yellow resin distn. residue, softening at 90-100°, after adjustment of the pH to >7 by aqueous Na2CO3, and extraction with CHCl3. A paper printing foil is coated with 2 parts by weight resin in 30 parts by volume EtOAc and 1 part 1% Rhodamine B solution. After processing the plate, the resin is removed from areas not covered by resinous toner by wiping with 5% H3PO4 and rinsing with water, whereby the hydrophilic paper is bared for use as a printing plate.

ACCESSION NUMBER: 1966:100028 CAPLUS
 DOCUMENT NUMBER: 64:100028
 ORIGINAL REFERENCE NO.: 64:18786b-d
 TITLE: Amine-aldehyde resins as photoconductors for electrophotographic processes
 INVENTOR(S): Lind, Erwin
 PATENT ASSIGNEE(S): Azoplate Corp.
 SOURCE: 4 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3244517		19660405	US	
PRIORITY APPLN. INFO.:			DE	19600917

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 6406403		19641207	NL	
PRIORITY APPLN. INFO.:			US	19630606

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L7 ANSWER 21 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
tolylquinazoline, me. 166' (from p-ClC₆H₄NH₂) 6-chloro-3-(p-
ClC₆H₄NH)CH₂C₆H₄(NHCO)Cl-2,5 [originally formulated by Miller and Wagner
CA 35, 28958] as 6-chloro-3-(p-ClC₆H₄phenyl)-3,4-dihydro-1(2H)-
quinazolinemethanellol, me. 140'. [EONH] (picrate me. 187-8').
[p-ClC₆H₄NHMe] 117-119. [127-129]. 1 g. I + 1 g. diisidine, and
110 ml. 98% H₂SO₄ stirred at 10-20° for 2 hrs. gave XVII (R = NH₂,
R' = Me) (XVIII). 219-220' (xylene). Similarly, 12 g.
O-dianisidine condensed with I in H₂SO₄ afforded 1.4 g. XVII (R = NH₂, R'
= Me), me. 285-6'. XVIII (1 g.) acetylated at room temp. with 5 ml.
CS₂H₆N and 2 ml. Ac₂O produced XVII (R = NHAc, R' = Me), me. >350'.
and, 1 g. XVIII refluxed 2 hrs. in 10 ml. Ac₂O gave 4,4'-diacetamido-5,5'-
diethyl-2,2'-biphenyldimideimide diacetate, me. 275 (decomp.).
XXI added to XXII gave 16% XVII (R = H, R' = Me), and 36% H₂O,
and the mixt. treated with KI produced 0.3 g. XVII (R = R' = Me), me.
216-17'. Reaction of I with arylamines having a free p-position in
acidified Na₂S₂O₃ soln. gave derivs. of [3,4-R₂(R₁N)C₆H₃CH₂2Sn (XX) and
(PhCNH₂)₂Sn. Thus, 25 g. Na₂S₂O₃, 25 ml. H₂O, and 8 ml. 40% I added to 10
g. PhNH₂ and 50 ml. 5M HCl and the mixt. heated 4 hrs. at 100° gave
7-5 g. XX, 22-24%. XXI, R₂ = H, R₁ = n-propyl, 4% (decomp.).
and 4 g. (p-H₂NC₆H₄CH₂)₂Sn = 103-5'. Similar condensations
using o-MeC₆H₄-NH₂, PhNHMe, and PhNHMe₂ produced XX, ZHC1 (R = R₁ = H, R₂ =
Me, n = 4), me. 225' (decomp.). (free base me. 139') [and
[3,4-Me₂(HN)C₆H₃CH₂]₂Sn me. 155'], XX (R₂ = H, R₁ = Me, n = 1),
me. 55' (ditrinitro base me. 136'), and (p-Me₂NC₆H₄CH₂)₂Sn
(XXI), me. 62', resp. XXI distd. at 11 mm. decompd. to
H₂S, p-Me₂NC₆H₄NHMe₂, and p-Me₂NC₆H₄CH₂: C₆H₄NHMe₂-p. XXI refluxed 30 min.
with Cu-bromide in EtOH-Li₂-triethylbenzene produced p-
Me₂NC₆H₄-CH₂-C₆H₄NHMe₂.

L7 ANSWER 22 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB To a cooled solution of 500 g. 40% aqueous MeNH₂ was added 258 g.
 2-(N-benzyl-
 N-methylamino)ethyl chloride hydrochloride and the mixture
 stirred 1 hr. at room temperature. The mixture was heated at 80-90° 3 hrs.,
 cooled, treated portionwise with 200 g. NaOH, and extracted with Et₂O to
 give
 137 g. N-benzyl-N,N'-dimethylethylenediamine (I), b.p. 5.
 .apprx. 80-2°. A solution of 175 g. I in 500 ml. CHCl₃ was added
 dropwise to a solution of 261 g. α-chlorodiphenylacetyl chloride in 1
 l. CHCl₃ at 20-5°. The mixture was refluxed 1 hr., then treated
 dropwise with 500 ml. absolute EtOH while distilling 1400 ml. solvent.
 The residue was refluxed 8 hrs. with 1500 ml. absolute EtOH to give 427 g.
 N-[2-(N'-benzyl-N'-methylamino)ethyl]-2-ethoxy-
 N-methyl-2,2-diphenylacetamide hydrochloride (II) m.
 162-4° (MeOH/Et₂O). A warm solution of 35 g. II was treated with a
 suspension of 3 g. 5% Pd-C at 55 lb.-30 min. to give 24.7 g. 2-ethoxy-
 N-methyl-N-(2-methylaminoethyl)-2,2-diphenylacetamide;
 hydrochloride (III) m. 202-3° (absolute EtOH). A suspension of 25 g.
 III and 200 ml. H₂O was treated with 3 g. NaOH in 30 ml. H₂O and the mixture
 extracted with Et₂O to give 19.5 g. 2-ethoxy-N-methyl
 N-(2-methylaminoethyl)-2,2-diphenylacetamide (IV), m. 459°. A
 mixture of 12.0 g. IV, 5.7 g. phenacyl chloride, and 250 ml. xylene was
 refluxed 15 min., cooled, and filtered and the filtrate treated with 4 ml.
 5N alc. HCl to give 7 g. 2-ethoxy-N-methyl
 N-(2-methylphenacylamino)ethyl-2,2-diphenylacetamide; hydrochloride (V)
 m. about 187-8°. A suspension 4.1 g. V in 20 ml. 50% EtOH was
 treated with 0.4 g. NaOH in 30 ml. 95% alc. followed by 0.4 g. NaBH₄. The
 mixture was stirred 10 min., then extracted with ether, and the ether
 extract
 treated with 2 ml. alc. HCl to give 3.5 g. 2-ethoxy-N-[2-[(β-
 hydroxyphenethyl)methylamino]ethyl]-N-methyl-
 2,2-diphenylacetamide hydrochloride (VI), m. 162-4°. VI was also
 prepared by treating IV with styrene oxide. 2-Ethoxy-N-[2-
 [(β-hydroxy-4-nitrophenethyl)methylamino]ethyl]-N-
 methyl-2,2-diphenylacetamide hydrochloride was hydrogenated to
 give N-[2-[p-amino-β-hydroxyphenethyl)methylamino]ethyl]-2-ethoxy-
 N-methyl-2,2-diphenylacetamide; dihydrochloride m.
 about 130-2°. The title compds. are useful as analgesics.
 ACCESSION NUMBER: 1964:468972 CAPLUS
 DOCUMENT NUMBER: 61:68972
 ORIGINAL REFERENCE NO.: 61:11938b-f
 TITLE: Diphenylacetamide derivatives
 INVENTOR(S): Krapcho, John
 PATENT ASSIGNOR(S): Olin Mathieson Chemical Corp.
 SOURCE: 3 pp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3143555		19640804	US	19620305

L7 ANSWER 24 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Compds. 1,2-BrClO₆SM, where X = Cl (I), SCN (II), H₂CCOME (III), CH₂CCOPH
 (IV), 4-HOCH₂CH₂CH₂ (V), 2,4-(HO)₂CH₂CH₂ (VI), 4,1-HOClO₆ (VII), 2,1-HOClO₆
 (VIII), NH₂ (IX), PhCH₂NH (X), PhNH (XI), 1-ClOH₂NH (XII), 4,1-H₂NC1O₆H
 (XIII), 2-ClOH₂NH (XIV), 2,1-H₂NC1O₆H (XV), 4-Me₂NC₆H₄ (XVI), 4-Et₂NC₆H₄
 (XVII), cyano (XVIII), AcO (XIX), and 1,2-BrClO₆SO₂ (XX) were prepared;
 also R₂NH (XXI), 1,2,4-H₂NC1O₆SR₂ (XXII), 1,2-RC1O₆NH₂ (XXIII), and R₂O
 (XXIV) (R = 2-ClOH₂TS). 1-Bromo-2-naphthylsulfonic acid, m. 135°
 (Cohen and Smiles, CA 23, 2172), was obtained in 86% yield.
 Bis(1-bromo-2-naphthyl)disulfide (4.76 g.) in CCl₄ treated with 0.8 g.
 anhydrous Cl₂, then filtered, and the filtrate concentrated gave 96% I, m.
 93-4° (decomposition). I (2.73 g.) in 40 ml. C₆H₆ treated with 1.45 g.
 anhydrous KSCN 1 hr. at 25-30° gave quant. II, m. 77-8° (petr.
 ether). I (1.36 g.), treated with 20 ml. anhydrous Me₂CO, gave quant. III,
 m. 72-3° (petr. ether). III was also obtained from II and Me₂CO,
 after 24 hrs. at room temperature I (1.36 g.) in C₆H₆ treated with 3 ml.
 PhCOMe
 and the excess steam distilled, gave 80% IV, m. 120-20.5°
 (petr. ether). II gave also with PhCOMe after 24 hrs. at room temperature
 IV in
 74% yield. I (1.4 g.) treated with freshly distilled PhOH, then
 with dilute NaOH, the insol. filtered off, the filtrate precipitated with
 dilute
 dilute H₂SO₄, filtered off, and recrystd. gave 41% V, m. 107.8-9° (petr.
 ether). The acetate, m. 92.8-4.2° (petr. ether), was obtained with
 Ac₂O and concentrated H₂SO₄. I (2.04 g.) in 30 ml. CHCl₃ added to 0.92 g.
 resorcinol in 3 ml. anhydrous Et₂O, the excess removed with boiling H₂O gave
 90% VI, m. 157-8.4° (C₆H₆-petr. ether). This gave with Ac₂O and
 concentrated H₂SO₄ the diacetate, m. 92.4-3.6° (petr. ether), in 87%
 yield. VI was also obtained in 90% yield from II and resorcinol after 48
 hrs. at room temperature I (1.3 g.) added to α-naphthol in C₆H₆ gave 93%
 VII, m. 131.5-2.3° (petr. ether); acetate m. 136-6.8° (petr.
 ether). Attempts to condense II with α-naphthol failed.
 β-Naphthol (1.08 g.) added to 2.04 g. I in 15 ml. C₆H₆ gave 91% VIII,
 m. 155-6° (petr. ether); acetate m. 119-20° (petr. ether).
 I dissolved in CHCl₃-Et₂O and treated with anhydrous NH₃ gave IX, but the
 crude product was very difficult to purify. II (4.8 g.) in Et₂O-CHCl₃
 solution treated with ethereal NH₃, the solvent removed, and the residue
 crystallized from petr. ether, gave 90% IX, decomposed at 90-205°. BzH
 (0.60 g.) added to 1.47 g. IX in 150 ml. MeOH gave in 70% yield X, m.
 114.4-15° (MeOH). I (1.36 g.) in 20 ml. C₆H₆ treated with 0.93 g.
 PhNH₂ in 5 ml. C₆H₆ gave 97% XI, m. 129-30° (petr. ether). I (2.73
 g.) in 30 ml. C₆H₆ was added to α-naphthylamine (2.86 g.)
 in 20 ml. C₆H₆, filtered, and the filtrate evaporated to an oily residue
 which
 gave 75% XII, m. 138-9° (decomposition) (petr. ether). II (1.48 g.)
 added to 1.43 g. α-naphthylamine, in 40 ml. C₆H₆,
 filtered, and the filtrate evaporated, to an oily residue, which was
 crystallized
 from C₆H₆-petr. ether to give quant. XIII (isomer of XII), m.
 157.2-9.2° (MeOH). I (1.36 g.) in 20 ml. C₆H₆ added to 1.43 g.
 β-naphthylamine in 10 ml. C₆H₆, then concentrated gave in 95%
 yield XIV, m. 137-8° (C₆H₆-petr. ether). XV.HCl was obtained in
 89% yield from 3.23 g. I in 200 ml. AcOH treated with 1.69 g. β-
 naphthylamine in 15 ml. AcOH. This, triturated with EtOH and 10%
 Na₂CO₃ gave the base, m. 199.2-200.4° (C₆H₆-petr. ether). II (0.74
 g.) added to 0.72 g. β-naphthylamine in 40 ml. C₆H₆, then
 concentrated gave 97% XV. XV in 48% yield was obtained from 0.37 g. I in
 20 ml.
 AcOH and 0.18 g. β-naphthylamine, 48 hrs. at room temperature

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 GI For diagram(s), see printed CA issue.
 AB A mixture of 50 g. aniline, 20 g. paraformaldehyde in 100 ml. 80% MeOH, and
 5 g. AcONa was heated 2 hrs. at 60°, kept overnight, and filtered
 to give 40 g. condensate (I). I (40 g.) in 100 ml. C₆H₆ was boiled and the
 mixture filtered and cooled to give 25 g. II, m. 140° (C₆H₆). To a
 mixture of 38 g. aniline, 10 g. EtOH, and 10 g. KOH was added 6 g.
 paraformaldehyde with stirring. The mixture was stirred 2 hrs. at
 60-70°, kept overnight, and filtered to give (PhNH)₂CH₂ (III), m.
 64-5° (iso-Pr₂O). The benzene-insol. portion of I was washed with
 C₆H₆ and CHCl₃ to give 3 g. [N(Ph)CH₂]_n (IV), m. 208°. II or IV
 (10 g.) in 50 ml. MeOH of C₆H₆ was hydrogenated (80 atmospheric H for 8
 hrs. at
 80°) and filtered. Ac₂O was added to the reduction product and the
 mixture heated 1 hr. at 60°, cooled, and filtered to give
 acetanilide, m. 114° (MeOH). The filtrate was distilled and
 separated into 2 fractions (V and VI), b.p. 52-6° and b.p. 102-5°,
 resp. V was identified as N,N-dimethylaniline as follows: V was heated
 with MeI to give PhMe₃NI, m. 211° (MeOH). Cooling of VI gave
 N-methylacetanilide, m. 105° (MeOH). Similarly,
 catalytic reduction of III gave a 1:1 mixture of PhNH₂ and PhNHMe.
 ACCESSION NUMBER: 1963:435276 CAPLUS
 DOCUMENT NUMBER: 59:35276
 ORIGINAL REFERENCE NO.: 59:6280g-h,6281a
 TITLE: Catalytic reduction of aniline-formaldehyde
 condensates
 AUTHOR(S): Wakae, Masao; Konishi, Kenzo
 CORPORATE SOURCE: Ind. Res. Inst., Osaka, Japan
 SOURCE: Osaka-furitsu Kogyo Shoreikan Hokoku (1963), No. 29,
 47-50
 CODEN: OFKSA; ISSN: 0369-7223
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 24 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 XVI, m. 136.8-7.8° (petr. ether), was obtained in 99% yield from
 2.04 g. I and 2.30 g. PhNH₂ in C₆H₆ soln., then treated with 5 ml. 10%
 Na₂CO₃, and the excess PhMe₂ steam distd. XVI was also
 obtained from II and PhNH₂. PhNH₂ (1.87 g.) added to 1.36 g. I in 15
 ml. C₆H₆ gave a ppt. This and the soln. were treated with 5 ml. 5% Na₂CO₃
 and the excess of reagents steam distd. to give 99% XVII, m.
 140.2-0.9° (petr. ether). XVII was also prepd. from II and PhNH₂.
 I (1.0 g.) or II in 20 ml. EtOAc treated with excess KCN, then with AcOH
 (10 ml.) gave XVIII, m. 142.8-3.8° (petr. ether). XIX, m.
 44-8°, was obtained in 82% yield from 1.66 g. AgOAc suspended in 10
 ml. abs. MeOH treated with 1.36 g. I, stirred 1 hr., then filtered, and
 the filtrate concd. 1-Bromo-2-naphthylsulfonic acid in NH₄OH, treated
 with aq. AgNO₃ gave the silver salt of the sulfonic acid. This (1.49 g.),
 suspended in C₆H₆ added to 1.02 g. I in C₆H₆ gave AgCl ppt., which was
 filtered off, and the filtrate concd. to give 73% XX, m. 174-5°
 (C₆H₆-petr. ether). XXI was obtained quant. from 1.0 g. IX treated with
 50 ml. AcOH, m. 208-9° (decompn.) (C₂H₅Cl₄-C₆H₆). XXII.HCl was
 obtained in 86% yield from 2.06 g. I in 150 ml. AcOH treated with 0.54 g.
 α-naphthylamine in 20 ml. AcOH. This, triturated with 10%
 Na₂CO₃ gave XXII, m. 239-40° (decompn.). XXII diacetate was
 obtained from XXII treated with Ac₂O-NaOAc, m. 189-92.5°
 (CCl₄-petr. ether). XXIII (0.95 g.) in 15 ml. C₆H₆ treated with 0.74 g. II
 in 10 ml. C₆H₆, left several days at room temp., and the solvent evapd.,
 gave in 98% yield XXIII. XXIII (0.47 g.) in 50 ml. C₆H₆ treated with 0.77
 g. I in 10 ml. C₆H₆, gave after 3 days XXIII. XXIII in 98% yield, was
 prepd. from 0.95 g. XIII in 30 ml. AcOH and 0.68 g. I in 50 ml. AcOH. The
 hydrochloride obtained, treated with MeOH and 10% Na₂CO₃ liberated the
 base. I (0.68 g.) in 70 ml. AcOH treated with 0.71 g. α-
 naphthylamine in 20 ml. AcOH gave after 2 days at room temp. 31%
 XXIII. XV (2.84 g.) in 40 ml. C₆H₆ added to 1.02 g. I, then filtered, and
 the filtrate concd., gave quant. XXIII, m. 186-7° (decompn.)
 (C₆H₆-petr. ether). XXIV, m. 145° (decompn.), was obtained in 90%
 and 66% yield resp. from 2.0 g. I and II, resp., in 60 ml. petr. ether
 stirred with N Na₂CO₃, and the obtained ppt. filtered off and dried. To
 prove the reactivity of some of synthesized compds. the following
 reactions were run. XII (0.5 g.) suspended in 15 ml. CCl₄, treated with
 anhyd. HCl gave quant. α-naphthylamine-HCl. This was
 filtered off and the filtrate concd. Half of the residue dissolved in
 AcOH, treated with KI aq. soln., liberated iodine. The remainder treated
 with Me₂CO gave III. II, treated with 10% NaOH gave bis(1-bromo-2-
 naphthyl) disulfide. This was filtered off and from the filtrate, treated
 with dil. H₂SO₄, was obtained 1-bromo-2-naphthylsulfonic acid. XXIV (0.5
 g.) moistened with EtOH, treated with 5 ml. N NaOH, gave a ppt. which was
 filtered off and recrystd. from CCl₄ to give bis(1-bromo-2-naphthyl)
 disulfide. The filtrate treated with dil. H₂SO₄ gave 1-bromo-2-
 naphthylsulfonic acid.
 ACCESSION NUMBER: 1963:3155 CAPLUS
 DOCUMENT NUMBER: 58:3155
 ORIGINAL REFERENCE NO.: 58:485a-h,486a-c
 TITLE: Reactivity of 1-bromo-2-naphthalenesulfonyl chloride
 and thiocyanate
 AUTHOR(S): Pitombo, Luiz R. M.
 CORPORATE SOURCE: Univ. Sao Paulo, Brazil
 SOURCE: Univ. Sao Paulo, Fapesp, Filsof., Cienc. Letras, Bol.
 Quim. (1959), (No. 5), 39-73
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 25 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Products containing the group R'N(CH₂CH(R)O)nH, in which R is H or Me, R' is an alkyl, cycloalkyl, aryl, or aralkyl group, and n is 1-10, are made as described in the main patent. Thus, 538 g. tetraethoxyaniline, 151 g. N-methyl-N-hydroxyethylaniline, and 100 g. paraformaldehyde were heated to 80-90° under CO₂. Then 8 g. H₃PO₄ was added slowly, whereupon the aldehyde was dissolved. After 1-2 hrs. at 80-90°, all H₂O was distilled off in a vacuum, and the condensation was continued until the desired viscosity was obtained. The product was a dark oil with a OH number of 369 and a viscosity of 496 cp. at 75°. N-Butyl-N-hydroxyethylaniline was also used, and p-toluenesulfonic acid may be used as a catalyst.

ACCESSION NUMBER: 1961:40739 CAPLUS
 DOCUMENT NUMBER: 55:40739
 ORIGINAL REFERENCE NO.: 55:79221, 7923a
 TITLE: Condensation polymers
 INVENTOR(S): Muller, Erwin; Bayer, Otto
 PATENT ASSIGNEE(S): Farbenfabriken Bayer Akt.-Ges.
 SOURCE: Addn. to Ger. 1,048,411 (CA 55, 2201a)
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1060140		19590625	DE	

L7 ANSWER 26 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 AB Et₂O layers dried over solid KOH, distd., and fractionated to yield 10.7% IX, 72.8% VIII, and 9.2% V. Picric acid with IV gave III picrate. 2,5-Furandimethanol diacetate (XV), m. 62-4° (ligroine), was prep'd. in 70% yield by heating 31 g. dimethylaminomethylfurfuryl alc., 4 g. anhyd. NaOAc, and 51 g. Ac₂O for 2 hrs. at 100°, neutralizing with Na₂CO₃, and extg. with Et₂O. XV (42.5 g.) was heated at 100° for 2 hrs. with 100 ml. EtOH and 30 g. KOH, 100 ml. H₂O added, and the soln. extd. with benzene, dried over K₂CO₃, distd., and chilled to yield 44.1% 2,5-furandimethanol (XVI), m. 73-4° (ligroine). XVI in acid soln. formed a resinous product insol. in org. solvents. VII (8.2 g.) was added dropwise with stirring to 15 g. HCHO, 1 ml. concd. HCl, and 25 ml. EtOH at 35-40°, stirred for 1 hr., dild. with 100 ml. H₂O, and extd. with Et₂O. After drying over CaCl₂ and distg., 30% IX was obtained. Similarly, 8.2 g. VII, 10 g. 45% AcH, and 2 ml. HCl gave 88% 1,1-bis(5-methyl-2-furyl)ethane, b₁₀ 108-10°, n_D 1.4992, and 25 g. AcH in prep'd. from 17 g. VII, 28 g. Me₂NH.HCl in 100 ml. MeOH, and 25 g. AcH in 43.2% yield; 48.8% VII was recovered.

ACCESSION NUMBER: 1960:80573 CAPLUS
 DOCUMENT NUMBER: 54:80573
 ORIGINAL REFERENCE NO.: 54:15349g-1, 15350a-g
 TITLE: Reactions of furan derivatives and formaldehyde
 AUTHOR(S): Tsuboyama, Kaoru; Yanagita, Masaya
 SOURCE: Scientific Papers of the Institute of Physical and Chemical Research (Japan) (1959), 53, 318-28
 CODEN: SPIPAG; ISSN: 0020-3092
 DOCUMENT TYPE: Journal
 LANGUAGE: English

L7 ANSWER 26 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The reactions of 2-substituted primary and secondary furfurylamine derivatives with HCHO were shown to produce hexahydrotriazines and methylenediamines, resp.; tertiary furfurylamines and their alkyl halides reacted with Ac₂O to give furfuryl acetates. Furfurylamine (I), b₁₇ 54-6°, n_D 1.4908 (I picrate m. 177.5-8.5°), was prepared in 70% yield by refluxing 17 g. furfural oxime, 12 g. Al (as Al-Hg), and 300 ml. EtOH 5 hrs., filtering off Al(OH)₃, adding 60 ml. 3N HCl, distilling, adding 30 ml. 30% NaOH, extracting with Et₂O, drying over solid KOH, distilling, and fractionating the residue. A mixture of 9.7 g. I and 8.0 g. 37% HCHO was heated on a water bath 2 hrs., extracted with Et₂O, and distilled to yield N,N',N''-trifurfurylhexahydrotriazine. The Schiff base prepared from 20 g. furfural (II) and MeNH₂ was reduced in EtOH 10 hrs. by Na-Hg. After removal of the Hg, the mixture was steam-distilled, and 20 ml. concentrated HCl added to the distillate. Unreacted II was removed by steam distillation, the residue made strongly alkaline with NaOH, extracted with Et₂O, dried over solid KOH, distilled, and fractionated to yield 68% N-methylfurfurylamine (III), b₆₉ 79-80°, n_D 1.4729; III-HCl, m. 144.5-6.0°; III picrate, m. 143.5-4.5°. Methylenabis(N-methylfurfurylamine) (IV) (79%), b₆ 126-8°, d₂₀ 1.0450, n_D 1.5017, was prepared from 8 g. 37% HCHO and 11 g. II. IV, on steam distillation with picric acid and EtOH, gave quant. yields of HCHO and III picrate. N,N-dimethylfurfurylamine (V), b₇₃ 72-4°, n_D 1.4609, was prepared in 69% yield by the reaction of a mixture of 58 g. HCONH₂ and 25 g. 80% HCO₂H with 20 g. II in 60 g. HCO₂H; V picrate, m. 101-2°. V (10 g.) was refluxed on a H₂O bath 3 hrs. with 10 g. Ac₂O, cooled, added to 100 ml. H₂O, and neutralized with Na₂CO₃ to form 87% furfuryl acetate (VI), b₂₁ 70-3°, n_D 1.4627. Similarly, VI was obtained from N,N,N-trimethylfurfuryl ammonium iodide with Ac₂O and NaOAc. Attempted reaction of V.HCl with HCHO did not yield condensation product; the higher the temperature, the smaller the amount of unreacted V recovered, and the greater the amount of resinous product formed. MeNH₂.HCl (65 g.), 41 g. 2-methylfuran (VII), and 50 g. 37% HCHO gave 24.6% N,5-dimethylfurfurylamine (VIII), b_{6,5} 51-5°, d₂₀ 1.09762, n_D 1.4803 (VIII.HCl, m. 140.5-1.5°; VIII picrate, m. 155.5-7.0°), 4.8% bis(5-methyl-2-furyl)methane (IX), b_{6,5} 90-3°, d₂₀ 1.0424, n_D 1.5018, 43.8% N-methyl-bis(5-methylfurfuryl)amine (X), b_{6,5} 129-32°, d₂₀ 1.0302, n_D 1.5040 (X picrate, m. 91-3°), and traces of methylenabis(N,5-dimethylfurfurylamine) (XI), b_{6,5} 141-4°, d₂₀ 1.0112, n_D 1.4998 (XI picrate, m. 155-6°). XI was prepared from IV and HCHO in 73% yield. Reaction of XI with picric acid gave quant. yields of HCHO and VIII picrate. The reaction of 20 g. VII with 25 g. HCHO and 25 g. MeNH₂.HCl gave 72.8% N,N,5-trimethylfurfurylamine (XII), b₂₈ 70-3°, n_D 1.4620; XII picrate, m. 115-16°; N,N,5-trimethyl-N-methylfurfuryl ammonium iodide, m. 160-2°. N,N,5-Trimethyl-N-methylfurfuryl ammonium bromide (XIII), m. 130-2° (EtOH-EtOAc), was prepared in 82% yield by refluxing 7 g. XII, 7 g. EtBr, and 10 ml. EtOH for 2.5 hrs., distilling, and extracting with Et₂O. 5-Methylfurfuryl acetate (XIV), b₇ 81-4°, n_D 1.4669, was prepared in 72% yield by heating XII with Ac₂O for 2 hrs. at 92-5°, from XIII, NaOAc, and Ac₂O in 86% yield. XII with HCHO gave 85% recovered XII; a resinous product, insol. in H₂O or Et₂O, was obtained in acid solution III (60 g.), 41 g. VII, 65 g. 37% HCHO, and 150 ml. 65% AcOH was refluxed 4 hrs., 400 ml. 25% NaOH added, the aqueous layer extracted with Et₂O, the organic and

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 AB 2-Arylaminothiophenyl aryl sulfides (I) and 1,3,5-triaryl-1,5-dithia-3-azapentanes were prepared by condensing primary aromatic amines with HCHO and thiophenols. N-Methylaniline condensed with HCHO and thiophenols to form N-methyl-N-arylaminothiophenyl aryl sulfides (Ia). Two arylaminothiophenyl aryl sulfides were prepared by condensing p-chloroethylaniline (II) with Na salt of the thiophenol. Basicities of these arylaminoalkyl aryl sulfides were related to the presence of electrophilic substituents attached to the aryl groups and the number of atoms separating the N and S atoms.

2,4,6-Trimethylbenzenesulfonyl chloride reduced with Zn and H₂SO₄ gave 2,4,6-trimethylbenzenethiol (thiomesitol). Nitrating mesitylene gave the nitro compound, and reduction of this compound gave 77% 2,4,6-trimethylaniline, b. 230-4°. p-Anisidine converted to N-methyl-p-methoxyacetanilide, treated with NaNO₂ and HCl to give N-nitroso-N-methyl-p-anisidine, and the nitroso group removed gave N-methyl-p-anisidine. Treating p-chloroethylaniline with concentrated HCl and SOCl₂ in CHCl₃ gave a product, m. 155-60°. I (Ar1NHCH₂SAr2) were prepared generally with 0.1 mole of the thiophenol, 0.1 mole primary aromatic amine, 0.1 mole 35-40% HCHO, and 20 ml. 95% alc.; the mixture was heated 2 hrs. at 80° refrigerated if crystallization did not occur, the immiscible oil extracted with Et₂O, and distilled in vacuo. These compds. were purified by recrystn. from ligroine. In the synthesis involving pentachlorothiophenol, C₆H₅ or PhMe was used as solvent and paraformaldehyde replaced HCHO. The following results were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 52-4.5°, 56; Ph, p-ClC₆H₄, 62-3.5°, 16; p-ClC₆H₄, p-ClC₆H₄, 66-2.7°, 33; o-ClC₆H₄, Ph, - (b₁ 120-2°), 28; o-ClC₆H₄, p-ClC₆H₄, 64-5°, 86; m-ClC₆H₄, p-ClC₆H₄, 62.5-4.5°, 23; Ph, 2,4,6-Me₃C₆H₂, 68-70.8°, 19; 2,4,6-Me₃C₆H₂, 2,4,6-Me₃C₆H₂, 157-9.2°, 67; p-MeOC₆H₄, p-ClC₆H₄, 73.6-5.6°, 21; p-MeOC₆H₄, p-ClC₆H₄, 113-15°, -; p-O₂NC₆H₄, p-ClC₆H₄, 139-41.5°, 74; Ph, C₆Cl₅, 125-35°, 46 (crude), 1a (Ar1MeCH₂SAr2) were prepared by the same general method as I by condensing 0.1 mole of the thiophenol and 0.1 mole of the N-methylaniline with 0.1-0.17 mole 35-40% HCHO in 20 ml. alc.; the resulting solid products, with the exceptions noted, were recrystd. from ligroine. Ia formed neither picrates nor p-nitrobenzoates. The following Ia were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 36.4-8°, 71; Ph, p-ClC₆H₄, 44.6-6.7°, 72; Ph, 2,4,6-Me₃C₆H₂, 51.8-2.8°, 89; Ph, C₆Cl₅, 118-21.4°, 91; p-O₂NC₆H₄, p-ClC₆H₄, 91.8-3.6°, 66; p-MeOC₆H₄, p-ClC₆H₄, 56.6-8.2°, 93. 1,3,5-Triaryl-1,5-dithia-3-azapentanes (Ar1SCH₂NAr2CH₂SAr1) (III) were obtained as follows. Thiophenol (0.1 mole), 0.05 mole PhNH₂, 0.1 mole 35-40% HCHO, and 20 ml. alc. heated 2 hrs. at 80° with stirring, the immiscible oils separated (crystallized on standing), and the resulting solids recrystd. from ligroine gave III. The following III were obtained (Ar1, Ar2, m.p., and % yield given): Ph, Ph, 50.2-2.2°, 56; p-ClC₆H₄, Ph, 60.6-61.4°, 74; p-ClC₆H₄, 113-15°, 71-4°, - (obtained as a byproduct in the preparation of the corresponding I and is probably contaminated). PhCH₂NH₂ (0.1 mole), 0.1 mole p-ClC₆H₄SH, and 0.1 mole 35-40% HCHO in 20 ml. alc. gave 8 g. mixture, m. 54-5.6°, picrate m. 81-145°. A small amount of N-benzylanilinomethyl p-chlorophenyl sulfide was obtained from the mother liquors, m. 71-3°. p-Chloroethylaniline.HCl (10 g.) and sufficient H₂O for solution was treated with 4.1 g. anhydrous K₂CO₃ and the solution extracted with Et₂O. p-Chlorothiophenol (0.06 mole) in 20 ml. alc.

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 added to 3 g. Na in 100 ml. alc. and then refluxed 2 hrs. with the filtered soln. of β -chloroethylaniline, the pptd. NaCl removed, the alc. and Et2O evapd., the solid residue dissolved in Et2O, extd. with 200 ml. 10% HCl, the solid floating between the layers sepd., slurried with H2O, treated with 10% NaOH followed by extn. with Et2O, the acid wash H2O treated with 10% NaOH, the solid that sepd. extd. with Et2O, the ext. combined with the other Et2O exts., dried, evapd., the residue dissolved in MeOH, and cooled gave 381 N-phenylamino-ethyl p-coblorophenyl sulfide, m. 45.2-6.6°, picrate m. 126.8-7.6°. Following the same procedure but using thiophenol gave a yellow oil following the neutralization of the HCl ext. with 10% NaOH; this oil in Et2O dried and evapd. gave 12.1 g. oil, which treated with Nuchar gave 214 N-phenylaminoethyl phenyl sulfide, m. 35-41° (ligroine). Infrared spectra were obtained for a no. of the above compds. The following observations were made from the infrared spectra. In support of the sulfide structure the SH peak at 3.7-3.9 μ was absent; in the N-arylaminoethyl aryl sulfides a sharp spike occurred at 2.9 μ , characteristic of the NH stretching in secondary amines; at 8 μ the peak showed aromatic amines; a band at 7.4-7.6 and a triplet at 8.1-8.5 μ were characteristic of tertiary amines; a triplet at 10 μ was also characteristic of the tertiary amines; spectra of 2,4,6-trimethylphenylaminoethyl 2,4,6-trimethylphenyl sulfide indicated a definite existence of steric hindrance. Potentiometric titrations of I (Ar1 = Ph, Ph, Ph, Ph, Ar2 = Ph, p-ClC6H4, 2,4,6-Me3C6H2, C6Cl5) with HClO4 in AcOH gave points at acid vols. that represented neutralization equivs. approx. double the formula wt. When the neutralization equiv. of the 2nd compd. was detd. by conductometric titration using the same HClO4 in AcOH the equiv. was equal to the formula wt. Placing a MeO or Me group p- or m- groups in the 2, 4, or 6-positions to the amine in I apparently increased the basicity. When a Cl atom was o, m, or p to the amine group the condensation product was neutral towards HClO4 in AcOH. A p-NO2 group also produced a neutral compd. Cl was not only o-p directing but also deactivated the ring. It was thought that steric effects played an important role in the case of the compd. prepd. from thiomethyl and mesidine. The o-Me groups on the amine and thiol nucleus made it more difficult for the protonating agent to attack the N atom. The 1,3,5-triaryl-1,5-dithia-3-azapentanes were neutral when titrated with HClO4 in AcOH. The electron withdrawal of the 2 thiomethyl and an aryl group reduced the basicity of the N atom so that the tertiary amine was neutral.

ACCESSION NUMBER: 1969:62378 CAPLUS
 DOCUMENT NUMBER: 53:62378
 ORIGINAL REFERENCE NO.: 54:55301, 5531a-1, 5532a-c
 TITLE: Condensation of thiophenols and formaldehyde with some aromatic amines
 AUTHOR(S): Grillo, Gerald F.; Schaffrath, Robert E.
 CORPORATE SOURCE: Syracuse Univ., Syracuse, NY
 SOURCE: Journal of Organic Chemistry (1959) 1035-8
 CODEN: JOCEAH ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 29 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Abietic acid (I) was condensed with EtCOOH (III) solution to give 518 8,9-bis(methylene)propionylabietic acid (IV), isolated as the cyclohexylamine salt (V). Hydrolysis of V afforded 8,9-dimethylolabietic acid (VI). The structure of VI was established by catalytic dehydrogenation to 1,8,10-trimethyl-2-isopropylphenanthrene (VII) and comparison with the totally synthesized compound. All attempts to cause I to react with II in aqueous solution or in inert solvents such as diisopropyl ether or p-dioxane failed; I could be recovered unchanged in each case. Similarly attempts to condense I with HCHO in the presence of 10% H2SO4 gave unchanged material. Aqueous NaH2PO4 used in excess was found to be a good reagent for the regeneration of I from its amine salt. Purified I showed $[\alpha]_D^{25}$ -101.6°. I (10g.) and 1 g. HCHO suspended in 50 ml. dioxane, 3 g. concentrated H2SO4 added and the temperature kept 0.5 hr. at 60°, 300 ml. H2O added, and the precipitate collected and dried gave a product which could not be crystallized. Expts. similar to the above were run using 2, 3, and 5 moles I/mole I. These products showed neutralization equivs. of 357, 394, and 419, resp., but a crystalline product could not be obtained. The product from the condensation of I with 2 moles II showed no maximum in the 220-285 μ region. Use of H3PO4 and BF3.Et2O gave similar results. I (10 g.) in 50 ml. dioxane was treated with 1 g. concentrated H2SO4, 10 ml. aliquots drawn at intervals and the content of I estimated from the absorption at 241 μ . I (3 g., $[\alpha]_D^{25}$ -101.6°) in AcOH refluxed 18 hrs. gave 2.7 g. I, $[\alpha]_D^{25}$ -100.4°. I (10 g.), 2.2 g. II, and 50 ml. AcOH refluxed 18 hrs., the AcOH distilled, and the residue taken up in Et2O gave a glass which could not be crystallized. Aliquots of a solution of 20 g. of the condensation product in 40 ml. Me2CO were treated at reflux with an equivalent amount of the following amines: Pr2, iso-Pr2, Bu, sec-Bu, iso-Bu, Bu2, iso-Bu2, 1-amino-2-hydroxypropane, 2-amino-1-hydroxy-2-methylpropane, Am, iso-Am, Am2, PhCH2, N-methylbenzyl, cyclohexyl, and piperidine. Cyclohexylamine produced a crystalline salt (VIII) after 1 min., whereas the other amines failed to crystallize after 30 days at 7°. This salt on purification m. 185°, λ 251.5 μ , ν 5.76 and 6.40 μ . VIII (5 g.) suspended in 100 ml. Et2O shaken with 20 g. NaH2PO4 in 100 ml. H2O, the Et2O layer separated, washed, dried, and concentrated gave 95% 8,9-bis(methylene)acetoxy)abietic acid (IX), m. 73-5° (sealed capillary) (C7H16), λ 251.5 μ , ν 5.76 and 5.88 μ . IX (25 g.) refluxed 2.5 hrs. with 15 g. KOH in 70 ml. H2O and 70 ml. alc., the cooled solution shaken with 300 ml. Et2O and 20 g. NaH2PO4 in 300 ml. H2O, the Et2O layer washed, dried, and distilled and the amorphous solid crystallized gave 11.5 g. VI, m. 192-3° (alc.), λ 251.5 μ , ν 24,200, $[\alpha]_D^{25}$ 143.2°. I (150 g.), 33 g. II, and 750 ml. III refluxed 20 hrs., excess III removed, and the residue taken up in Et2O, washed, dried, and distilled gave a yellow glass which could not be crystallized. This crude IV was dissolved in 350 ml. Me2CO and refluxed with 100 g. cyclohexylamine, left at 7° overnight, the crude salt collected, and recrystd. to give 145 g. V, m. 175° (ligroine), $[\alpha]_D^{25}$ 85.6°, λ 251.5 μ . IV was liberated from V and subsequent basic hydrolysis as described above gave VI identical with the above prepared specimen. Treatment of VI with tosyl chloride in CSHSN gave a yellow solid showing infrared spectrum bands at 5.75 and 5.88 μ . There also appeared to be OH absorption at 3.0 μ . VI (32 g.) treated with CH2N2 and then

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 AB cf. C.A. 52, 284c. Tertiary amines containing aromatic groups are brominated in the nucleus; with ease and in good yields by N-bromosuccinimide (I); aromatic amines are substituted under these conditions exclusively in the p-positions. Amines of this type undergo with Ph(OAc)4 (II) in Ac2O oxidative dealkylation. (PhCH2)3N (28.7 g.) in 150 cc. dry C6H6 treated at 20-30° with stirring with 18 g. I in portions, the mixture heated 0.5 hr. at 80°, poured into iced H2O, and filtered gave 25 g. (PhCH2)2NH.HBr, m. 246-8°, the C6H6 layer yielded 10 g. BzH. iso-PrMeNPh (14.9 g.) in 80 cc. dry C6H6 and 18 g. I allowed to stand 5 min., filtered, evaporated, and distilled yielded 14 g. p-BrC6H4NMeCHMe2, b2 105°, m. 32-4°. A series of similar runs were performed with the following amines (products and % yield given): Et3N, AcH and Et2NH, - (1 hr. reaction time); Ph3N, p-BrC6H4NPh2, 50 (3 hrs. reaction time); 1-ClO7NHMe (III), 4-Br derivative of III, 70; 2-ClO7NH2 (IV), 1-Br derivative of IV, -; PhNET2 (V), p-Br derivative of V, -; PhMeNCH2Ph, p-BrC6H4NMeCH2Ph, 85 (5 min. reaction time); (PhCH2)2NHPh, p-BrC6H4N(CH2Ph)2, 82. p-O2NC6H4NMe2 and PhNMe2.EtBr did not react under these conditions. PhNMe2 (6 g.) in 25 cc. CHCl3 and 10 cc. Ac2O treated dropwise under N during 30-40 min. with 22.15 g. II in 50 cc. CHCl3, the mixture stirred 1 hr. with occasional cooling and filtered, the CHCl3 layer washed with 200 cc. H2O, the combined aqueous solns. treated with 50 cc. 2N H2SO4, filtered, and the filtrate treated with 2,4-(O2N)2C6H3NHNH2 gave 614 H2O derivative; the CHCl3 layer evaporated in vacuo gave 6.1 g. MePhNAC, m. 102°. Similar dealkylations with II were performed using the following tertiary amines (% yields of aldehyde and N-ac derivative of the secondary amine, product, and m.p. of product given): PhNET2, 93, 90, EtPhNAC, 51; p-MeC6H4NMe2, 91, 87, p-MeC6H4NACMe, 82; p-MeOC6H4NMe2, 80, 82, p-MeOC6H4NACMe, 78 (resin formation); p-ClC6H4NMe2, 66, 56, p-ClC6H4NACMe, 91; p-O2NC6H4NMe2, 51, 82, p-O2NC6H4NACMe, 151; 2-ClO7NHMe2, 27, 22, 2-ClO7NHACMe, 50° (strong resinification); p-Me2NC6H4CHO, 50, 44, p-OHCC6H4NACMe, 56° (p-Me2NC6H4)2CO (VI), 71, 90, p-AcMeNC6H4COCC6H4NMe2-p, 137°. VI, 2 mole equivs. II, 50 cc. CHCl3, and 20 cc. Ac2O yielded similarly 35% (p-AcMeNC6H4)2CO, m. 92°.

ACCESSION NUMBER: 1959:62378 CAPLUS
 DOCUMENT NUMBER: 53:62378
 ORIGINAL REFERENCE NO.: 53:11277g-1, 11278a-c
 TITLE: The course of substitution. XIV. The reaction of tertiary amines with N-bromosuccinimide and lead tetraacetate
 AUTHOR(S): Horner, Leopold; Winkelmann, Erhard; Knapp, Karl H.; Ludwig, Werner
 CORPORATE SOURCE: Univ. Mainz, Germany
 SOURCE: Chemische Berichte (1959), 92, 288-92
 CODEN: CHBERH ISSN: 0009-2940
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 53:62378

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 dissolved in 200 ml. CSHSN and treated 2.5 hrs. at 0° with 33.5 g. tosyl chloride, 30 ml. H2O added portionwise during 0.5 hr., the suspension poured into 200 ml. H2O, extd. with CHCl3, the exts. washed, dried, and distd. gave 44 g. of the diosylate (X) of the Me ester of VI, ν 7.28, 8.40, 8.48, 10.45, and 14.28 μ , all attributed to the tosylate functions. X (40 g.) in Et2O added dropwise to 7.5 g. LiAlH4 and 200 ml. Et2O, refluxed 1 hr., decompd. with EtOAc, the mixt. treated with NH4Cl, and distd. gave 23 g. of a product which showed infrared bands characteristic of the tosylate function; reduction of the carbomethoxy group to methylol appeared to be complete. This material dissolved in 200 ml. Bu2O added to 7 g. LiAlH4 in 100 ml. Et2O, the mixt. refluxed 3 hrs., and worked up as above gave 16 g. of a product which gave no bands for the tosylate function, but there was some absorption in the carbonyl region and fairly strong bands at 8.50 and 8.74 μ . This substance may be a mixt. of 8,9-dimethylabietinol and the cyclic ether. This mixt. (10.5 g.) treated with tosyl chloride gave a tosyl deriv. which was reduced with LiAlH4 in Bu2O to give 6.2 g. yellow oil, which showed no OH absorption but still showed strong absorption at 8.50 and 9.74 μ indicating the presence of the ether function. Dehydrogenation of 2 g. VI over 2 g. 10% Pd-C 4 hrs. at 300-30° gave 0.2 g. of the trinitrobenzene complex of retene, m. 143-4°. No other product was isolated. VI (10 g.) in 100 ml. MeOH catalytically reduced 24 hrs. at 50 lb./sq. in. over 2 g. 10% Pd-C and worked up gave a solid which could not be recrystd. from the common solvents; it had no ultraviolet absorption in the 220-85 μ region. 8,9-Dimethyloltetrahydroabietic acid (4 g.) dehydrogenated 4.25 hrs. at 300-30° over CO2 over 2 g. 10% Pd-C, cooled, extd. with Et2O, filtered, and evapd. gave a residue, treated with picric acid to give 2.2 g. VII picrate, m. 177-8° (alc.). The picrate in 100 ml. Et2O shaken with 250 ml. portions 10% Na2CO3 gave 0.83 g. VII, m. 84-5° (MeOH). Na (31 g.) in 600 ml. alc. treated with 238 g. MeCH(CO2Et)2, then 260 g. o-bromo-o-xylene added dropwise so as to maintain reflux, the mixt. refluxed 4 hrs. longer, decompd., the crude ester refluxed 8 hrs. in 200 ml. H2O with 200 g. KOH, the clear soln. washed with Et2O, treated with 500 ml. 10% H2SO4, refluxed 5 hrs., the org. layer sepd., and the exts. combined, washed, dried, and distd. gave 152 g. α -methyl- β -(o-tolyl)propionic acid (XI), b3 147-50°; amide, m. 109-10°. XI (152 g.), 120 g. alc., 300 ml. C6H6, and 3 ml. concd. H2SO4, refluxed 8 hrs. under a Dean and Stark H2O trap, and distd. gave 156 g. XI Et ester (XII), b1.5 97-9°. XII (156 g.) in 350 ml. Et2O added dropwise during 1 hr. to 28 g. LiAlH4 and 800 ml. Et2O, decompd. with EtOAc, then with 10% HCl gave 118 g. 2-methyl-1-(o-tolyl)-1-hydroxypropane (XIII), b1.5 101-2°. XIII (110 g.) and 200 g. CSHSN treated dropwise between 0-5° with 85 g. PBr3, stirred 0.5 hr. at 5°, 200 ml. Et2O added, the stirring continued 1 hr. at 5°, left at room temp. overnight, H2O added, extd. with Et2O, and the exts. washed with 100 ml. 10% HCl, then with H2O, dried, and distd. gave 114 g. 1-bromo-2-methyl-3-(o-tolyl)propane (XIV), b1 95-6°. XIV refluxed 40 hrs. with 38 g. KCN in 150 ml. H2O and 50 ml. alc., cooled, didd. with 400 ml. H2O, the org. layer sepd., refluxed with 70 g. KOH in 140 ml. H2O, cooled, treated with 70 g. concd. H2SO4 in 200 ml. H2O, extd. with Et2O, and distd. gave 60 g. β -methyl- γ -(o-tolyl)butyric acid (XV), b1.5 151-3°, p-tolulide, m. 107-8°. XI (100 g.) and 140 g. SOCl2 left overnight gave after a 1-hr. reflux 102 g. α -methyl- β -(o-tolyl)propionyl chloride (XVI), b3 120-1°. XVI (100 g.) in 250 ml. Et2O left 15 min. at 5-10° with CH2N2 in Et2O, left at room temp. overnight, the Et2O removed, the crude product dissolved in 500 ml. dioxane, treated 1

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 hr. at 60° with 10 g. Ag₂O, 25 g. Na₂CO₃, and 1.5 g. Na₂S₂O₃ in 1
 l. H₂O, refluxed 2 min., cooled, treated with 25 g. Na₂CO₃, extd. with
 Et₂O, and the ext. distd. gave 49.6g. XV. XV (45 g.) and 100 g.
 SOCl₂ left overnight at room temp. and refluxed 1 hr. gave 46 g.
 β-methyl-γ-(o-tolyl)butyryl chloride (XVII), b_p 131-2°, XVII (38.7 g.) in 40 ml. ligroine added to 35 g. AlCl₃ and
 after the initial reaction, the system refluxed 2 hrs., the complex
 decomp. by addn. of 10% HCl at 5°, the org. layer sepd., and
 distd. gave 24 g. 3,5-dimethyl-1-tetrahydronaphthalenone (XIX),
 b_p 118-20°, m. 63-4°. XIX (22 g.) and 22 g. BrCH₂CO₂Et in
 50 ml. each C₆H₆ and PhMe treated with 9 g. Zn and a crystal of iodine,
 after the reaction began the remainder of the soln. added, an addnl. 9 g.
 Zn and 10 g. BrCH₂CO₂Et added, and refluxing continued 3 hrs., cold, dil.
 HCl added, and the org. layer extd. with C₆H₆ gave 5.3 g. unreacted XIX
 and 14.2 g. Et 1-(3,5-dimethyl-3,4-dihydronaphthyl)acetate (XX), b_p
 156-8°. XX (2.16 g.), 1.90 g. N-bromosuccinimide, and 20 ml. CHCl₃
 refluxed 3 hrs., the system cooled, filtered, and distd. gave a
 residue which heated 2 hrs. in vacuo on the H₂O bath gave a material
 showing no CO absorption in the infrared, m. 46-9°, picrate, m.
 140-1°. XX (14 g.) in 150 ml. MeOH acidified with 2 drops concd.
 HCl and hydrogenated 12 hrs. at 25° and 50 lb./sq. in. with 10%
 Pd-C gave 10.5 g. Et 1-(3,5-dimethyl-1,2,3,4-tetrahydronaphthyl)acetate
 (XXI), b_p 142-3°. XXI (11 g.) dehydrogenated 9 hrs. under N at
 320° over 1 g. 10% Pd-C with evolution of 2100 ml. H₂ gave 8.9 g. Et
 1-(3,5-dimethylnaphthyl)acetate (XXII), b_p 156-8°. XXII (8.9 g.)
 in 30 ml. Et₂O added dropwise to 5 g. LiAlH₄ in 50 ml. Et₂O, excess LiAlH₄
 destroyed, dil. HCl added and the Et₂O phase sepd., and washed gave the
 crude alc. This alc. treated at 5-10° with 5.5 g. PBr₃ and left 4
 hrs. at room temp. gave 8.6 g. 1-bromo-2-(3,5-dimethyl-1-naphthyl)ethane
 (XXIII), b_p 173-5°. XXIII (26 g.) added slowly to a refluxing
 soln. of the Na salt of iso-PrCH(CO₂Et)₂ (from 2.4 g. Na, 21 g.
 iso-PrCH(CO₂Et)₂ and 4.8 g. alc. in 60 ml. PhMe), the mixt. refluxed 12
 hrs., the PhMe removed, the residual oil taken up in Et₂O, washed, evapd.,
 and the residue refluxed 8 hrs. with 20 g. KOH and 20 ml. H₂O, cooled,
 treated with 15 ml. H₂O, extd. with C₆H₆, and the clear soln. treated
 cautiously with 50 ml. 10N H₂SO₄, refluxed 6 hrs., and extd. gave 8.3 g.
 α-isopropyl-γ-(3,5-dimethyl-1-naphthyl)butyric acid (XXIV),
 b_p 225-7°. XXIV (4.5 g.) in 20 ml. C₆H₆ left 1 hr. at room temp.
 with 4.3 g. PCl₅, heated 5 min. on the H₂O bath, cooled to 5°, 4.5
 ml. SnCl₄ added, the system left 15 min. at 5°, decomp. with acid,
 the org. phase sepd., and the C₆H₆ evapd. gave 3.8 g. 8,10-dimethyl-2-
 isopropyl-1-oxo-1,2,3,4-tetrahydronaphthene (XXV), m. 56-8°
 (MeOH). XXV (3 g.) in 15 ml. Et₂O added at 5° to MeMgI (from 7 g.
 MeI) in Et₂O, left overnight, poured into cold dil. HCl, the Et₂O layer
 sepd. and the Et₂O evapd. gave a residue which dehydrogenated by heating
 1.5 hrs. at 310° over 1 g. 10% Pd-C under N, the system cooled, the
 product taken up in Et₂O, and the solvent evapd. gave 2.6 g. VII, m.
 85-6°, picrate, m. 175-6°. A mixt. of this synthetic VII
 was identical with the product isolated from dehydrogenation of the
 abietic acid deriv. The mixed m.p. of the picrates was 175-7°.

ACCESSION NUMBER: 1959:34684 CAPLUS
 DOCUMENT NUMBER: 53:34684
 ORIGINAL REFERENCE NO.: 53:6177d-1,6178a-1,6179a-f
 TITLE: Condensation of abietic acid with formaldehyde
 AUTHOR(S): Royals, E. Earl; Greene, Joseph L., Jr.
 CORPORATE SOURCE: Emory Univ., Emory Univ., GA
 SOURCE: Journal of Organic Chemistry (1958), 23, 1437-43
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal

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 AB cf. C.A. 51, 113541. Et₂NCH₂CO₂ (I), b_p 71-2°, and styrene were
 made to react in 2:1 mole ratio by blowing in BF₃ below 10° until
 approx. 2 moles BF₃ is absorbed, stirred 30 hrs. at room temperature,
 extracted with
 Et₂O, and distilled to give a joint compound, Et₂N(CH₂)₂CHPhOBu, b_p 75-
 89-90°, HCl salt, m. 151-2°. Similarly, 64 g. I and 10 g.
 ethylene oxide in the presence of 40 g. BF₃ gave 4 g. Et₂NCH₂CO₂(CH₂)₂OBu,
 b_p 76.5-7.0°, and 2 g. Et₂NCH₂CO₂(CH₂)₂OBu, b_p 116°. Et₂NCH₂CO₂(CH₂)₂OBu
 (II) was treated with ketene by blowing in the latter with
 cooling in the presence of ZnCl₂, extracting, and distilling to give the
 corresponding 2 joint compds.: the low-boiling compound was a
 β-aminopropionic ester and the high-boiling, an amide (R and R' of
 II, b.p. or m.p. of both products, and % yields given): Et, Et, b_p 115-
 75-6°, 9.72%, b_p 103-6°, 35.2%; Et, Bu, b_p 93.5-4.5°,
 9.95, b_p 103-5° 20.0; [R₂ = O(CH₂-CH₂)₂, Bu, b_p 117-18°,
 14.0, m. 89-93°, 3.5; [R₂ = (CH₂)₅, Bu, b_p 5.101-2°, 18.8,
 m. 37-41°, 53.6. R₂NCH₂CH₂ gave similarly the joint compds. with
 ketene (R, b.p. and % yield given): Et, b_p 103-6°, 40.0; [R₂ =
 O(CH₂CH₂)₂], b_p 187-9°, 57.9; [R₂ = (CH₂)₅], b_p 148-55°.
 77.4. Joint compound of benzoic amide and NaHSO₃ with HCHO (PhCONHCH₂CH₂SO₃Na)
 (7 g.) was treated with 18 g. PhCONH₂ in the presence of EtONa at
 190-200° to give 84% PhCONHCH₂CH₂SO₃Na, m. 219.0-19.5°.
 Similar reactions with phthalimide gave 51% PhCONHCH₂CH₂(CO)₂C₆H₄-o,
 m. 183-4°, and with carbazole, 49% PhCONHCH₂CH₂(C₆H₄)₂, m.
 199.0-9.5°.

ACCESSION NUMBER: 1959:29086 CAPLUS
 DOCUMENT NUMBER: 53:29086
 ORIGINAL REFERENCE NO.: 53:5262b-e
 TITLE: Joint reaction and trans jointing
 AUTHOR(S): Oda, Ryohsei; Tanimoto, Shigeo; Nomura, Motoaki;
 Nishimura, Tsunehiko; Kyo, Kayomon
 CORPORATE SOURCE: Kyoto Univ.
 SOURCE: Kogyo Kagaku Zasshi (1957), 60, 18-20
 CODEN: KGKZA7; ISSN: 0368-5462
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 29 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 53:34684

L7 ANSWER 31 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 GI For diagram(s), see printed CA Issue.
 AB A solution of 40% NaHSO₃ (1 mole) ice-cooled, 40% CH₂O added, the mixture
 stirred 2 hrs., warmed at 25-30°, 1 mole MeNH₂ added, stirring
 continued 2 hrs., 1 mole KCN added, the mixture stirred 2 hrs., then
 extracted
 with Et₂O, and the extract distilled gave 54% MeNHCH₂CH₂CO₂ (I), b_p 70°,
 n_D 1.4081. Similarly, other RNHCH₂CH₂CO₂ (II) were prepared (R,
 b.p./mm., n_D/t°, and yield shown): Et, 81°/29,
 1.4370/35°, 56; Pr, 91°/20, 1.4370/35°, 65; iso-Pr,
 80°/29, 1.4179/23°, 70; and Bu, 105°/29,
 1.4226/36°, 66. Reduction of the II with LiAlH₄ gave the compds.
 RNH(CH₂)₂NH₂ (R, b.p., n_D/t°, and % yield shown): Me,
 115-16°, 1.4391/24°, 54; Et, 128-9°,
 1.4396/24°, 61; Pr, 147-50°, 1.4331/31°, 55; iso-Pr,
 136-7°, 1.4420/19°, 74; and Bu, 169-72°,
 1.4368/30°, 65. EtNH(CH₂)₂NH₂ (3.3 g.) in 50 ml. CHCl₃ with 10.35
 g. K₂CO₃ treated dropwise with 3.97 g. AcCl in 15 ml. CHCl₃ with ice
 cooling, and the mixture stirred 1 hr. gave 4.0 g. AcEtN(CH₂)₂NHAc, b_p
 180°, n_D 1.4711. Similarly, MeNH(CH₂)₂NH₂ with Et₂NCOCl gave 60%
 Et₂NAcN(CH₂)₂NHCONEt₂, b_p 202°, n_D 1.4796. HCHO (35% weight/volume)
 added to a cooled solution of RNH(CH₂)₂NH₂ in C₆H₆, the mixture heated from
 80° to 100°, and the H₂O distilled gave the compds.
 (R, b.p./mm., n_D/t°, and % yield shown): Me, 113°/8,
 1.4788/24°, 67; Et, 130°/8, 1.4716/35°, 80; Pr,
 149°/8, 1.4681/32°, 62; and Bu, 160°/3,
 1.4693/30°, 60. iso-PrNH(CH₂)₂NH₂ (111) (4.05 g.) in 100 ml. C₆H₆
 treated with 2.85 g. PrCHO, stirred 5 hrs., and distilled gave 4.6
 g. 1-isopropyl-2-propylimidazoline (IV), b_p 100-121°, n_D 1.4540.
 EtO₂CCl (4.25 g.) in 20 ml. alc. added to 3.05 g. IV, 4.15 g. Na₂CO₃, and
 150 ml. alc. at reflux, the mixture stirred 5 hrs., cooled, filtered, the
 filtrate evaporated, and the residue dissolved in 30 ml. 5% NaOH and
 extracted
 with Et₂O gave EtO₂C (iso-Pr)N(CH₂)₂NHCO₂Et, b_p 160°, n_D 1.4449.
 A solution of 5.1 g. III in 50 ml. Et₂O cooled, 4.2 g. CS₂ added dropwise,
 the mixture stirred 1 hr., and the precipitate filtered, dried, and heated
 2 hrs.
 at 130-40° gave 5.2 g. 1-isopropyl-2-imidazolidinedithione (V), m.
 166°. V in PhMe with excess PhNCO at reflux 12 hrs. gave 90%
 1-isopropyl-3-phenylcarbamoyl-2-imidazolidinedithione, m. 104-5°.
 Similarly, 1-ethyl-3-phenylcarbamoyl-2-imidazolidinedithione, m.
 83-4°, and the 1-Bu homolog, m. 68-9°, were prepared
 1-ethyl-2-imidazolidinedithione (I g.) and 1.5 g. Et₂NCOCl heated 2 hrs. on
 a steam bath and 2 hrs. at 130°, and the mixture evaporated, treated with
 5% NaOH, and extracted with C₆H₆ gave 1-ethyl-3-diethylcarbamoyl-2-
 imidazolidinedithione.

ACCESSION NUMBER: 1958:88121 CAPLUS
 DOCUMENT NUMBER: 52:88121
 ORIGINAL REFERENCE NO.: 52:15549d-1
 TITLE: Studies in potential filaricides. II. Synthesis of
 substituted imidazolidines and 2-imidazolidinedithiones
 AUTHOR(S): Wadia, P. S.; Anand, Nitya; Dhar, M. L.
 CORPORATE SOURCE: Central Drug Research Inst., Lucknow
 SOURCE: Journal of Scientific & Industrial Research (1958),
 17B, 24-30
 CODEN: JSIRAC; ISSN: 0022-4456
 DOCUMENT TYPE: Journal
 LANGUAGE: English

L7 ANSWER 32 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Condensation products are obtained when an amide reacts with HCHO and a hexitylamine (produced by reduction of the corresponding hexosamine). Thus, 493 g. N-methylglucamine (I) (produced by the simultaneous reaction of glucose, H₂, and MeNH₂) and 505 g. of lauramide were dissolved in 1750 mL MeOH and 75 g. paraformaldehyde was added. The mixture was heated for 2 h. under reflux and the MeOH and the water of reaction were removed by distillation, first at atmospheric pressure and finally under a vacuum of 1-2 mm. at a maximum temperature of 125°. A firm, waxy condensation product remained in the pot. Other amides which were treated with I and HCHO were melamine, stearamide, oleamide, urea, phthalimide, and acetamide. The products are said to be useful as surfactants, antistatic and textile-finishing agents, corrosion inhibitors, lubricants, additives, waxes, and resins.

ACCESSION NUMBER: 1958:13648 CAPLUS
 DOCUMENT NUMBER: 52:13648
 ORIGINAL REFERENCE NO.: 52:2457a-c
 TITLE: Amide condensation products
 INVENTOR(S): Zech, John D.
 PATENT ASSIGNEE(S): Atlas Powder Co.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2813091	---	19571112	US	---

L7 ANSWER 33 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 CORPORATE SOURCE: Nomura, Motoaki; Suda, Hideaki; Matsuda, Kazuo
 SOURCE: Bulletin of the Institute for Chemical Research, Kyoto University (1955), 33, 117-25
 CODEN: BICRAS; ISSN: 0023-6071
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 33 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB cf. C.A. 51, 6528c. The β -sulfoethylations with Na isethionate of N-methylololeylamide, N,N'-distearoylthylenediamine*
 ** , 2-heptadecylindole, and 2-heptadecylbenzimidazole were conducted. The amount (g.) and name of starting compound, amount (g.) of Na isethionate, reaction temperature, reaction time, and yield (%) of purified product were: 10,
 ***N-methylololeylamide, 10, 220°, 13, 20; 8, N,N'-distearoylthylenediamine, 13, 210°, 11, 17; 3, 2-heptadecylindole, 3, 210°, 12, 33; 10, 2-heptadecylbenzimidazole, 8, 220°, 9, 30. As catalyst 0.3 g. powdered NaOH was used in every case and the products were recrystd. from alc. or water. Et orthoformate (50 g.) and 30 g. acetamide refluxed 15 hrs., cooled, filtered, and washed with acetone gave 23-27.7% MeCONHCH₂CH₂CO₂Me which showed no distinct m.p. after 3 recrystns. Similarly 27 g. Et orthoformate and 12 g. benzamide gave 9.2 g. PhCONHCH₂CH₂NCOPh, m. 207-8°. 8-methylolphthalimide and benzoic acid, both 0.1 mole, in 100 cc. 95% H₂SO₄ left 4 days at 10-15°, poured into water, the precipitate filtered off, extracted with NaOH solution, and acidified with HCl gave 17

g. m-phthalimidomethylbenzoic acid (I), m. 228.5-30.5° (from alc.). I was hydrolyzed by refluxing in 20% NaOH, acidified with HCl, filtered to remove phthalic acid, and the filtrate evaporated to dryness to give 88.5% m-aminomethylbenzoic acid hydrochloride, m. 250-1°; treatment with Amberlite IR-4B gave the free amine, m. 246-8°. Heating the free amine at 245-55° 5 hrs. gave a brittle and hard resin. Quinaldine (50 g.), 25 cc. water, 27 cc. EtOH, and 1.5 equivalent (37% solution) was refluxed 24 hrs., the solvent distilled, and the residual 2-hydroxyethylquinoline dehydrated to 7% 2-vinylquinoline (II) by distilling with 1.3 g. NaOH and 0.5 g. N-phenyl- β -naphthylamine. The β -(2-quinolinol)ethylations were successfully conducted from II with PhCOMe, PhCOEt, and CH₂(CO₂Et)₂. Vinyl Bu ether was heated 10 hrs. in the presence of p-toluenesulfonic acid as a catalyst with dialkylaminomethyl Bu ethers from piperidine, Et₂NH, and morpholine to give 72% C₅H₁₀CH₂CH₂CH(Obu)₂, b₅. 154-5°, 60% Et₂N(CH₂)₂(Obu)₂, b₄. 5 122-3°, and 77% CH₂CH₂CH₂CH₂CH₂CH(Obu)₂, b₅ 155-7°, resp. Hydrolysis of these aminoaldehyde acetals with HCl gave free aldehydes which readily polymerized. β -Piperidinopropionaldehyde di-Bu acetal in ether was treated with dry HCl and the precipitate collected quickly to give the free aldehyde hydrochloride, m. 133-6°. The 2,4-dinitrophenylhydrazones of this aminoaldehyde was obtained from the di-Bu acetal. That the last 3 reactions are transjointing has been shown. Another transjointing reaction with benzyl β -sulfoethyl ether was described. Benzyl β -sulfoethyl ether was prepared (70%) by adding 1.5 g. powdered NaOH to a refluxing mixture of 150 g. benzyl alc. and 45 g. Na isethionate and keeping at 180° 7 hrs. The transjointing reaction with malonic ester was conducted by adding 100 g. di-Et malonate to 50 cc. absolute alc. containing 1.3 g. Na, removing the solvent, adding 11 g. benzyl β -sulfoethyl ether, heating 20 hrs. at 170°, washing with ether, dissolving the residue in water, and acidifying; yield 25%. Similarly, transjointings with acetoacetic ester and aniline were performed in 20 and 22% yields, resp.

ACCESSION NUMBER: 1957:62378 CAPLUS
 DOCUMENT NUMBER: 51:62378
 ORIGINAL REFERENCE NO.: 51:11355b-1
 TITLE: Joint reaction and transjointing. III
 AUTHOR(S): Oda, Ryohei; Teramura, Kazuhiro; Tanimoto, Shigeo

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 AB cf. C.A. 50, 9211. HC(OEt)₃ (27 g.) and 12.0 g. BzNH₂ refluxed 12 hrs., cooled, and the solid washed with water and then with hot water yielded 8.2 g. BzNHCH₂NEt₂, m. 297-8°. Similarly 50 g. HC(OEt)₃ and 30 g. AcNH₂ gave 27% AcNHCH₂NAC, which readily decomposed CH₂(NHbz)₂ (50 g.) and 25 g. CH₂(NHAc)₂ heated gradually up to 270° and refluxed 9 hrs., the product added to 250 cc. water, extracted with ether and CHCl₃, and the insol. residue recrystd. from water repeatedly gave 2.0 g. BzNHCH₂NHAc, m. 179.5-81°. Transjointing between 11.5 g. 1,3-diphenylimidazolidine and 16.0 g. CH₂(CO₂Et)₂ with 2 g. CaCl₂ or ZnCl₂ as catalyst in EtOH produced 95% (PhNHCH₂)₂ and 53% (CH₂)₃(CO₂H)₂ (after decarboxylation). Similarly PhNMe₂ and 1,3-diphenylimidazolidine gave (p-Me₂NC₆H₄)₂CH₂ and β -naphthol and 1,3-diphenylimidazolidine gave 65% α,α' -methylenebis- β -naphthol. Refluxing 6 hrs. 38 g. CH₂(OCH₂Ph)₂, 23 g. CH₂(OEt)₂, and 3 g. ZnCl₂, treating the mixture with excess aqueous NaHCO₃, extracting with benzene, drying, and repeatedly distilling the benzene layer gave 8.9 g. EtOCH₂CH₂Ph, b₂₄ 105-11°. NaOEt from 3 g. Na, 16.5 g. BuOCH₂CH₂CN, and 9.5 g. Et₂NH were warmed at 40-50° 4 hrs., left overnight at room temperature, heated at 75° for a while, and neutralized with AcOH to give after fractionation by distillation 6.7 g. Et₂NCH₂CH₂CN, b₃₅ 102°. Similarly 25.4 g. BuOCH₂CH₂CN, 32 g. CH₂(CO₂Et)₂, and 4.6 g. Na gave 16 g. NCCH₂CHCH(CO₂Et)₂, b₅ 145-51°. NCCH₂CH₂NEt₂MeI (14 g.) and 43.5 g. morpholine heated 3 hrs. at 110° and distilled gave 3.5 g. β -morpholinopropionitrile, b₁₃ 130-3°; NCCH₂CH₂CH(CO₂Et)₂ was similarly obtained. PhBr (30 g.) was converted into PhMgBr, 15 g. CH₂(NEt)₂ added, and the mixture refluxed 4 hrs. From the reaction product, 4 g. PhCH₂NEt₂, b₁₅ 87°, was obtained; no PhCH₂ was detected even when excess Grignard reagent was used. Similarly PhCH₂MgCl (from 20 g. PhCH₂Cl) and 25 g. CH₂(NEt)₂ produced 15.3% PhCH₂CH₂NEt₂. The Grignard reagent from 31.4 g. PhBr added slowly to 16 g. Et₂NCH₂CH₂OBu gave 11.5 g. PhCH₂NEt₂, b₁₅ 90.5-91°. PhCH₂CH₂NEt₂ was also produced similarly in 91% yield. Et₂NCH₂CH₂OBu (29 g.) and 5.4 g. urea heated 20 min. and distilled gave 20 g. residue from which (Et₂NCH₂CH₂NH)₂CO was identified as picrate.

ACCESSION NUMBER: 1956:36075 CAPLUS
 DOCUMENT NUMBER: 50:36075
 ORIGINAL REFERENCE NO.: 50:7112b-g
 TITLE: Joint reaction and transjointing. II
 AUTHOR(S): Oda, Ryohei; Nomura, Motoaki; Tanimoto, Shigeo
 CORPORATE SOURCE: Kyoto Univ.
 SOURCE: Bulletin of the Institute for Chemical Research, Kyoto University (1954), 32, 231-7
 CODEN: BICRAS; ISSN: 0023-6071
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 35 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB New syntheses of 3-aryl-3-butenylamines, substituted cinnamylamines, and 1-aryl-3-aminopropanols by the reaction of substituted styrenes, CH₂O, and secondary amines in AcOH are reported. Unsatd. tertiary amines have been obtained from the reaction of several terpenes, CH₂O, and secondary amines. The appropriate amine (1 mole) in 400 cc. AcOH treated with 31.6 g. paraformaldehyde, the mixture heated until a clear solution was obtained, the solution treated with 1 mole of the appropriate amine, the mixture refluxed with stirring, poured into H₂O, and extracted with C₆H₆, the aqueous layer basified with excess NaOH and extracted with C₆H₆, and the extract dried and distilled gave the corresponding 3-aryl-3-butenylamine. In this manner were prepared the following compds. PhC(CH₂)₂(CH₂)₂X (X, b.p./mm., n_D²⁵, reaction time in hrs., and % yield given): Me₂NH (I), 65-70°/0.5, 1.5225, 16, 60 [(Me₂N)CH₂]₂ was used as the source of the amine and 50% of the required CH₂O; Et₂NH (II), 145-6°/25, 1.5126, 5, 33; morpholino (III), 175-80°/15, 1.5439, 16, 30; NMeCH₂Ph, 140-50°/1, 1.5615, 16, 39; the p-Me derivs. of I (IV), 115-20°/6, 1.5209, 6, 56; of II, 110-15°/2, 1.5156, 16, 34; of III, 160-5°/4, 1.5407, 16, 61; piperidino analog of IV, 145-8°/4, 1.5363, 16, 32; pyrrolidino analog of IV, 125-30°/2, 1.5384, 16, 18. Similar condensations with CH₂O were carried out with the following terpenes and secondary amines (b.p./mm., n_D²⁵, and % yield of the condensation product, and reaction time in hrs. given): α-pinene, Me₂NH, 120-30°/18, 1.4819, 33, 30; β-pinene, Me₂NH, 133-43°/20, 1.4771, 65, 2; camphene, Me₂NH, 55-65°/0.3, 1.4789, 21 (26% with Me₂NH.H₂SO₄), 16; d-limonene, Me₂NH, 70-80°/0.3, 1.4809, 24, 16; dipentene, piperidine, 105-14°/0.75, 1.5000, 22, 16; β-pinene, piperidine, 115-25°/2, 1.4977, 28, 16; camphene, morpholine, 87-97°/0.5, 1.5025, 24, 16; β-pinene, morpholine, 170-80°/10, 1.4985, 44, 16; d-limonene, morpholine, 100-10°/0.3, 1.5030, 18, 16. In the same manner were prepared the following amino alcs. Arch(OH)CH₂CH₂X (Ar, R, X, b.p./mm., n_D²⁵, & yield, and reaction time in hrs. given): p-MeOC₆H₄, H, morpholino, 175-85°/2.0, 1.5328, 36, 1; p-MeOC₆H₄, Me, Me₂NH, 130-40°/1.2, 1.5144, 42, 8; 3,4-CH₂O₂C₆H₃, Me, Me₂NH, 125-35°/0.4, 1.5241, 34, 8. I (75 g.) in 175 cc. EtOH hydrogenated at 100° and 100 atm. over 7 g. Raney Ni gave 59.5 g. Me₂N(CH₂)₂CHMePh, b_D 110-13°, n_D²⁵ 1.4940. p-MeOC₆H₄CH₂CH₂ (52 g.), 70 g. 76% tech. Me₂NH.H₂SO₄ solution, 13 g. 95% paraformaldehyde, and 72 g. AcOH refluxed 18 hrs. with stirring, the mixture cooled, poured into 500 cc. H₂O, and extracted with C₆H₆, the aqueous layer basified with excess aqueous NaOH and extracted with C₆H₆, and the C₆H₆ extract dried and distilled gave 48 g. distillate, b_D 110-35°, which redistd. yielded 22 g. p-MeOC₆H₄CH₂CH₂NHMe₂, b_D 120-5°. Paraformaldehyde (9 g.), 120 g. AcOH, 61.5 g. Me₂NH.H₂SO₄ heated with stirring and treated with 60 g. (p-MeOC₆H₄)₂CH₂, the mixture refluxed 16 hrs. with stirring, and the amine isolated in the usual manner and distilled gave 36 g. (p-MeOC₆H₄)₂CH₂CH₂NHMe₂, b_D 2.2 195-205°, n_D²⁵ 1.5853. HCl passed into 87.5 g. I in 216 g. PhOMe with stirring and cooling, the mixture heated to 80°, the resulting solution treated slowly with 70 g. ZnCl₂, the mixture treated 1 hr. with dry HCl, heated 2 hrs. at 120°, cooled, mixed with 1 l. H₂O, and 100 g. concentrated HCl, the aqueous layer basified with 500 cc. 50% aqueous NaOH and extracted with C₆H₆, and the C₆H₆ solution dried and

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 AB cf. C.A. 37, 96.7. An attempt to prepare N,N-dimethylhomoveratrylamine (I) from homoveratrylamine (II) or N-methylhomoveratrylamine by the Clarke-Eschweiler reaction gave mainly 2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III) (Clarke, et al., C.A. 28,98.9). Since the Pictet-Spengler reaction has not been observed in the absence of strong acid except with phenolic amines it seemed probable that II could be methylated with HCHO and HCO₂H if acidity were avoided. Despite these precautions, the yield of I was only 44%; in addition there was a 14% yield of III and a small amount of an isomer of III. Conclusion: the Pictet-Spengler reaction (Buck, C.A. 28, 6149.3) is considerably more facile than has been previously supposed and when the structural peculiarities of a phenethylamine are favorable, the Clarke-Eschweiler reaction cannot be manipulated to avoid the cyclization completely. HCHO (10 g.) added to 9.1 g. II in a steam bath, 2.4 cc. 90% HCO₂H added, the mixture heated to 87°, the pH held at about 7 by addns. of HCO₂H (about 5 cc. added during 3 hrs.), 5 cc. HCHO added, 3 cc. HCO₂H added in 1.5 hrs., the mixture heated 1.5 hrs. (final pH 5), the solution evaporated in vacuo, 7 cc. HCl added, the solution evaporated in vacuo, the residue dissolved in absolute EtOH and diluted with EtOAc yielded 1.7 g. III.HCl, m. 213-15° the mother liquors evaporated, the bases liberated, distilled in vacuo (below 1 mm.) yielded I; the undistd. bases (about 3 g.) yielded 0.8 g. material, C₁₂H₁₂NO₂.HCl, m. 229-30° (decomposition) (perhaps dimethoxy-N-methyltetrahydroisoquinoline -HCl), which with permanganate gave an unidentified acid. ACCESSION NUMBER: 1955:32414 CAPLUS DOCUMENT NUMBER: 49:32414 ORIGINAL REFERENCE NO.: 49:6263a-d TITLE: Competition between the Clarke-Eschweiler and Pictet-Spengler reactions AUTHOR(S): Baltzly, Richard CORPORATE SOURCE: Wellcome Research Labs., Tuckahoe, NY JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1953), 75, 6038-9 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal LANGUAGE: Unavailable

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 distd. yielded 103 g. p-MeOC₆H₄(CHMePh)(CH₂)₂NHMe₂, b_D 185-95°, n_D²⁵ 1.5564 ACCESSION NUMBER: 1956:24203 CAPLUS DOCUMENT NUMBER: 50:24203 ORIGINAL REFERENCE NO.: 50:4964f-1,4965a-d TITLE: The aminomethylation of olefins. I. The reaction of secondary amines, formaldehyde, and olefins. SCHMIDLE, Claude J.; Mansfield, Richard C. Rohm & Haas Co., Philadelphia, PA JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1955), 77, 4636-8 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal LANGUAGE: Unavailable OTHER SOURCE(S): CASREACT 50:24203

L7 ANSWER 37 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB cf. C.A. 43, 3425e. Condensation of phenols with HCHO and primary amines yields N,N-bis(hydroxybenzyl)amines directly in certain instances. The nature of the substituent ortho to the phenolic OH plays an important role in determining the course of the reaction. Infrared absorption spectra are given. MeNH₂ (0.2 mole) added (cooling) to 12 g. paraformaldehyde in 60 cc. MeOH containing 0.1 g. KOH, the mixture treated with 48.8 g. 2,4-Me₂CH₂CO₂H in 60 cc. MeOH, refluxed 2 hrs. and evaporated at room temperature yielded 51 g. N,N-bis(3,5-dimethyl-2-hydroxybenzyl)methylamine [α_D²⁰ (methylimino)dimesitol], m. 124-5° (all m.ps. uncor.). For other similarly prepared (3,5,6,2-R₁,R₂,R₃(HO)C₆H₃CH₂)₂NH, R, R₁, R₂, R₃, yield (%), m.p., and m.p. of the HCl salt are: cyclohexyl, Me, Me, H, 52, 146-7°, 213-15°; HOCH₂CH₂, Me, Me, H, 60, 128-9°, 185-6°; Me, Cl, Me₃C, H, 52, -, 169-71°; cyclohexyl, Cl, CH₃, H, 59, 167-8°, 149-50°; Me, Me₃C, Me₃C, Me, 55, 130-1°, -. Cyclohexylamine (9.9 g.) added portionwise with cooling to 10 cc. MeOH containing 6 g. paraformaldehyde and 0.05 g. KOH, the solution added to 30 g. p-Me₃CC₆H₄OH in 10 cc. MeOH, the mixture let stand 1 day at room temperature, 50 cc. C₆H₆, 8 g. NaOH, and 450 cc. water added, the aqueous layer extracted with C₆H₆, and the combined exts. evaporated in vacuo yielded 24.6 g. 3,4-dihydro-3-cyclohexyl-6-tert-butyl-1,3,2H-benzoxazine, m. 93-4°. Cyclohexylamine (4.95 g.) added to 3 g. paraformaldehyde in 8 cc. MeOH containing 0.05 g. KOH, the solution added to 17.3 g. p-BrC₆H₄OH in 15 cc. MeOH, the mixture let stand 18 hrs. at room temperature, and the solvent removed in vacuo yielded 35% 3,4-dihydro-3-cyclohexyl-6-bromo-1,3,2H-benzoxazine, m. 91-2°. Paraformaldehyde (2.4 g.) in 5 cc. MeOH containing 0.1 g. KOH (cooled) treated with 4.96 g. 25% MeNH₂, then with 7.4 g. 6-chlorothymol (Me = 1) in 8 cc. MeOH, the mixture refluxed 3 hrs., extracted with C₆H₆, and the C₆H₆ evaporated yielded 9 g. 3,4-dihydro-6-chloro-3,5-dimethyl-6-isopropyl-1,3,2H-benzoxazine (I), b_D 120-2°. I (2.2 g.), 5 cc. 20% HCl, and 25 cc. EtOH distd. (30 cc. 50% EtOH and 10 cc. water added during the distillation) until 20 cc. remained and the residue diluted with 20 cc. water yielded 1.1 g. N-methyl-5-chloro-2-hydroxy-6-methyl-3-isopropylbenzylamine-HCl (2-methylaminomethyl-6-chlorothymol-HCl), m. 172-4°. N,N-Bis(4-hydroxy-3,5-dimethoxybenzyl)cyclohexylamine (65% yield), m. 141°. N,N-Bis(4-hydroxy-3,5-dimethoxybenzyl)amine, m. 137°. ACCESSION NUMBER: 1953:54814 CAPLUS DOCUMENT NUMBER: 47:54814 ORIGINAL REFERENCE NO.: 47:9292a-e, 9293a TITLE: N,N-Bis(hydroxybenzyl)amines: synthesis from phenols, formaldehyde, and primary amines BURKE, W. J.; Smith, Richard P.; Weatherbee, Carl Univ. of Utah, Salt Lake City JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (1952), 74, 602-5 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal LANGUAGE: Unavailable OTHER SOURCE(S): CASREACT 47:54814

L7 ANSWER 38 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 AB The condensation of 2-C10H7OH (I) with formaldehyde and aliphatic and alicyclic primary amines yielded 2,3-dihydro-2-substituted-1H-naphth-[1,2-e]-m-oxazines (II) or N, N-bis(2-hydroxy-1-naphthylmethyl)alkylamines (III) depending upon the reaction conditions. The II were readily split by acids to yield the corresponding 1-(substituted aminomethyl)-2-naphthols. To 12.4 g. 25% aqueous MeNH₂ in 60 cc. MeOH were added with cooling 18.5 cc. 37% aqueous CH₂O in 40 cc. MeOH and 14.4 g. I in 50 cc. MeOH, and the mixture was gently refluxed 1.5 h. and poured into 400 cc. cold H₂O to yield 19.6 g. (98%) 2,3-dihydro-2-methyl-1H-naphth-[1,2-e]-m-oxazine (V), m. 67-8° (from MeOH); HCl salt, m. 185-7° (decomposition), obtained in quant. yield from V in cold Me₂CO with 1 equivalent concentrated HCl. The following II (2-alkyl group) were prepared similarly: PhCH₂ (VI), 99.5%, white prisms, m. 126-7° (from EtOH); HCl salt, m. 169-70° (decomposition); Bu, 87%, oil (HCl salt, m. 138-40°); cyclohexyl (VII), quant., oil (HCl salt, m. 178-9° (decomposition)). VII (4 g.) and 1.0 cc. concentrated HCl in 60 cc. 85% PrOH were distilled, while 25 cc. PrOH was being added, until the CH₂O was removed, 60 cc. Me₂CO was added, and the mixture cooled to give 3.65 g. (93%) 1-cyclohexylaminomethyl-2-naphthol-HCl, m. 192-3° (decomposition) (from EtOH). The following III-HCl (alkyl given) were prepared similarly: PhCH₂, 85%, m. 170-2° (from MeOH); Bu, 60%, m. 143-5° (from 50% aqueous MeOH); Me (VIII), 94%, m. 202-4° (decomposition) (from EtOH). To 28.8 g. I and 15 cc. 37% aqueous CH₂O in 75 cc. MeOH was added dropwise 12.4 g. 25% aqueous MeNH₂ in 50 cc. MeOH and the mixture let stand 24 h. at room temperature to give 31.2 g. (91%) 1,1'-bis(2-hydroxy-1-naphthyl)trimethylamine (IX), m. 147-8° (from HCONMe₂-MeOH); HCl salt + 1 mol. MeOH, m. 142-4° (from MeOH), from IX in MeOH and excess concentrated HCl; HCl salt, m. 148-51° (decomposition). Similarly were prepared the following III (alkyl given): Bu, 64%, white prisms, m. 137-8° (from HCONMe₂-MeOH); HCl salt, m. 135-7° (from aqueous MeOH); cyclohexyl (X), 86%, m. 120-2° (HCl salt, m. 172-4° (from MeOH)). The condensation of equimol. quantities of MeNH₂, CH₂O, and I at 25° gave 82% IX; similarly was obtained from cyclohexylamine (XI) 59% X. A 1:2:1-mol. ratio of MeNH₂-CH₂O-I condensed at 0° gave 79% IX and 20% V, at 25° 58% V and 39% IX. A similar condensation of a 1:2:2 mol. XI-CH₂O-VI mixture at 60° yielded 55% VII. To 1.0 g. VI in dry Et₂O was added a large excess of PhMgBr and the resulting precipitate in 15 cc. EtOH treated with 3 cc. concentrated HCl to yield 0.1 g. (8%) 2-HOClOH₆CH₂N(CH₂Ph)₂, m. 115-17°, also obtained in 62% yield by refluxing 1.5 h. 3 g. VIII and 8.0 g. (PhCH₂)₂NH₂ in 40 cc. EtOH. IX (3 g.), 12.4 g. 25% aqueous MeNH₂, and 15 cc. 37% CH₂O in 100 cc. MeOH gently refluxed 1.5 h. gave 3.4 g. (98%) V. In a similar run with PhCH₂NH₂, VI was obtained in 97% yield. To 5.8 g. IX in 70 cc. AcOH was added at 0° 2.3 cc. aqueous HNO₃ and after 5 min. 200 cc. H₂O to give 1,2-O₂NClOH₆OH, m. 102-3°. A similar nitration of IX at 25° gave 63% 1,6,2-(O₂N)2C1OH₅OH, m. 193-4°. IX (3.43 g.) treated 2 wk. at room temperature with 10 g. Ac₂O and 20 cc. pyridine, and the mixture poured into 200 cc. H₂O gave 4.3 g. diacetate (XII) of IX, m. 158-60° (from EtOH). Hydrolysis of XII with 2% KOH in MeOH at 25° gave IX. IX (5 g.) in 30 cc. Ac₂O heated 8 h. at 125°, and the mixture made alkaline with 2 g. excess KOH in 150 cc. MeOH, refluxed 2 h., cooled, and acidified with concentrated HCl precipitated 2.9 g. (68%) N-methyl-N-(2-hydroxy-1-naphthylmethyl)acetamide (XIII), m. 199-200° (from

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 AB The methylation of PhNH₂, o- (I) and p-MeC₆H₄NH₂ (II), 5,2-BrMeC₆H₃NH₂ (III), o-ClC₆H₄NH₂ (IV), and 2,6- (V) and 2,4-xylydine (VI) with (HCHO)n and HCO₂H, HCl, HBr, or AcOH, or without acid shows that, without acid, only negligible condensation takes place. Heating PhNH₂, (HCHO)n, and 98% HCO₂H (1:1:1) 1 hr. gives 92% (p-Me₂C₆H₄)₂CH₂, m. 85-6°; p-MeC₆H₄NH₂, (HCHO)n, and HCO₂H (1:1:1), heated 3.5 hrs., give 98% [5,2-Me(Me₂N)C₆H₃]₂CH₂. Heating V, (HCHO)n, and HCO₂H (1:3:3) 0.5 hr. gives 33% 2,6-Me₂C₆H₃NH₂, b.p. 194-9°, and 63% diphenylmethane base, b.p. 170-5°, m. 49.5-50.5°, resolidifying and m. again. 60-60.5°; 2,6-Br₂C₆H₃NH₂ (VII), (HCHO)₃, and HCO₂H (1:3:8), heated 3 hrs., give 83% [3,5,4-Br₂(H₂N)C₆H₂]₂CH₂, m. 159-60°; m-O₂NC₆H₄NH₂ (VIII), (HCHO)n, and HCO₂H (1:2:6:4), heated 10.5 hrs., give [4,2-Me₂(O₂N)C₆H₃]₂CH₂, m. 191-2°. II, (HCHO)n, and HCO₂H (1:3:3), heated 0.5 hr., give a trace of p-MeC₆H₄NH₂ and 10% 3-p-tolyl-6-methyl-3,4-dihydroquinazoline, m. 156.5-7°. VI (0.2 mol.) added to (HCHO)n and HCO₂H (1:3:3) reacts vigorously when the mixture is heated 0.5 hr. 33% 2,4-Me₂C₆H₃NH₂ and an unidentified compound, b.p. 8 186-7°, m. 165-6°, are formed. Similarly, 2,4-Cl₂C₆H₃NH₂ (IX), (HCHO)n, and HCO₂H (1:3:3) give 84% 2,4-Cl₂C₆H₃NH₂, m. 169.5-70.5°, which is changed when refluxed with Ac₂O alone or with CSH₅N. The rate of methylation is measured by determining the CO₂ formed. After an extensive study of the effect of the amount of HCHO, of H₂O, of variation in the ams. of HCO₂H, of strong acids, of the order of mixing the reagents, and of agitation, the results of which are given in 5 tables, a modified procedure for the Wallach methylation of aromatic amines is given: 1 mol. amine is added gradually to a gently warmed and stirred mixture of 2.5 mols. (HCHO)n and 3 mols. HCO₂H, the mixture heated 5 min. on a steam bath, poured into ice-cold NaOH (1.3 equivs. to 1 of the HCO₂H) and Na₂SO₃ (1.2 equivs. to 1 of the HCHO), the solution steam-distilled, and the distillate extracted with ether. In this way the following amines give the corresponding N,N-di-Me derive. (4 yield): I 40, II 50, IV 23, p-isomer 65, VI 65, V 97, p-O₂NC₆H₄NH₂ 50, p-MeC₆H₄NH₂ 50, mesidine 98, IX 92, VII 92, 2,4-Me₂C₆H₃NH₂ 98, 2,4,6-Br₃C₆H₂NH₂ 98, o-MeC₆H₄NH₂ 55, p-isomer 95, 2,4-Me₂C₆H₃NH₂ 98, 2,6-isomer 98. PhNH₂, m-MeC₆H₄NH₂, 1- and 2-ClOH₇NH₂, p-H₂N₂C₆H₄SO₃H, VIII, PhNHMe, and m-MeC₆H₄NHMe are not methylated by this procedure. The primary and secondary amines successfully methylated all have 1 or more of the o- and p-H atoms replaced. With all reactive positions unsubstituted, the nuclear condensations predominate; with 1 or 2 reactive positions blocked, methylation reaches 90% with all reactive positions blocked, methylation is almost 100%.
 ACCESSION NUMBER: 1953:28627 CAPLUS
 DOCUMENT NUMBER: 47:28627
 ORIGINAL REFERENCE NO.: 47:4854a-g
 TITLE: Methylation of aromatic amines by the Wallach method
 AUTHOR(S): Borkowski, Walter L.; Wagner, E. C.
 CORPORATE SOURCE: Univ. of Pennsylvania, Philadelphia
 SOURCE: Journal of Organic Chemistry (1952), 17, 1128-40
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 47:28627

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 AB EtOH), sol. in dil. aq. alkali, gives a greenish yellow color with alc. FeCl₃. XIII (2.9 g.) in 12 cc. Ac₂O heated 8 h. at 100-10° gave 3.1 g. (90%) O-Ac deriv., m. 123-5° (from aq. MeOH). The N-CH₂Ph analog of XIII, m. 169-70° (from EtOH), was prep'd. similarly in 37% yield from VI and Ac₂O at 130°. IX (3 g.) in 30 cc. H₂O contg. 4 g. KOH refluxed 30 min. and the mixt. dild. with 200 cc. H₂O and acidified with HCl gave 2.4 g. (2-HOClOH₆)₂CH₂, m. 202-3°. Condensation of 9.9 g. XI with 15 cc. 37% CH₂O in 100 cc. MeOH and 14.4 g. 1-ClOH₇OH in 100 cc. MeOH at -5 to 0° yielded 18.0 g. (67%) 3,4-dihydro-3-cyclohexyl-2H-naphthol[2,1-e]-m-oxazine (XIV), m. 86-8° (from Me₂CO), decompd. by heating in MeOH or Me₂CO. XIV (11.2 g.) and 5.0 cc. concd. HCl in 50 cc. EtOH refluxed 5 min. gave 79% 2-cyclohexylaminomethyl-1-naphthol-HCl (XV), m. 171-4° (decompn.). XV (1.2 g.) and 1.74 g. piperidine heated 30 min. at 100-10° and dild. with 10 cc. MeOH gave 71% 2-piperidinomethyl-1-naphthol, m. 133-4°.
 ACCESSION NUMBER: 1953:31863 CAPLUS
 DOCUMENT NUMBER: 47:31863
 ORIGINAL REFERENCE NO.: 47:5408b-1,5409a-h
 TITLE: Condensation of naphthols with formaldehyde and primary amines
 AUTHOR(S): Burke, W. J.; Kolbezen, Martin J.; Stephens, C. Wayne
 CORPORATE SOURCE: Univ. of Utah, Salt Lake City
 SOURCE: Journal of the American Chemical Society (1952), 74, 3601-5
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 47:31863

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 AB cf. C.A. 43, 3425e. Dropwise addition of 0.1 mole PhCH₂NH₂ to 0.22 mole aqueous 37% CH₂O in 50 cc. dioxane at 15-18°, then 0.03 mole phloroglucinol dihydrate, refluxing 1.5 hrs., evaporation of solvent, and crystallization of the residue from 9:1 C₆H₆-EtOH gave 48% 3,4,6,7,8,10,11,12-octahydro-3,7,11-tribenzyl-2H-benzo[1,2-e,3,4-e',5,6-e'']tris-m-oxazine, m. 162-3°, insol. in MeOH and 40% aqueous MeOH, partially soluble in hot EtOH, soluble in aqueous HCl, C₆H₆, and hot CCl₄ and EtOAc. A series of bis-m-benzoxazines was prepared similarly (read amine used, phenol, m.p., and % yield): MeNH₂, pyrocatechol, 174-5°, 45; PhCH₂NH₂, pyrocatechol, 182-3°, 48 (1a); cyclohexylamine, pyrocatechol, 143-4°, 29; MeNH₂, hydroquinone, 182-3°, 61; cyclohexylamine, hydroquinone, 161-2°, 31 (1b); PhCH₂NH₂, toluhydroquinone, 105°, 58. Solution of 0.4 g. 2,3,4,7,8,9-hexahydro-3,8-dimethylbenzo[1,2-e,4,5-e']bis-m-oxazine (I) in 20 cc. warm 95% EtOH, cooling, addition of 4 cc. concentrated HCl at 0°, and slow distillation of the EtOH with addition of 20 cc. H₂O gave 72% 2,5-bis(methylaminomethyl)hydroquinone-2HCl, m. 269-70° (from H₂O). The distillate contained CH₂O. Dropwise addition of 0.2 mole 85% HCO₂H to 0.011 mole I at 0°, then 3.8 cc. 37% CH₂O, heating to 90°, cooling to 70° during 30 min. (gas evolution), heating 2 hrs. at 90°, 12 hrs. at 85°, cooling, addition of 5 cc. concentrated HCl, concentration in vacuo to a solid, solution in aqueous Na₂CO₃ and extraction with EtOAc gave 71% 2,5-bis(dimethylaminomethyl)hydroquinone (IIa), m. 190-1°. Addition of 0.22 mole cyclohexylamine during 2 min. to 0.22 mole 37% CH₂O in 75 cc. dioxane, then 0.1 mole hydroquinone, refluxing 2.5 hrs., and concentration gave 35% 2,5-bis(cyclohexylaminomethyl)hydr oquinone (II), m. 173-4°. Addition of 0.0053 mole 37% CH₂O to 0.0015 mole II in 50 cc. cooled dioxane, 2 hrs. at 55°, 1 hr. at room temperature, and concentration gave 86% Ib. Ia (6 g.) and 15 cc. Ac₂O heated 2 hrs. at 90-5°, 2 hrs. at 80°, and allowed to stand 3 hrs. at room temperature gave a brown viscous precipitate; addition of excess NaHCO₃ and CHCl₃ extraction gave 3 g. 2,5-bis[(N-acetylcyclohexylamino)methyl]hydroquinone, m. 290° (decomposition). 2,5-Bis[(N-acetylmethylamino)methyl]hydroquinone, similarly prepared from I, m. 273-5°. MeMgBr gave no gas evolution with dry C₆H₆ solns. of I, Ia, or Ib, but did give a definite gas evolution with II and IIa. I and Ib gave no H with Na in C₆H₆.
 ACCESSION NUMBER: 1951:13892 CAPLUS
 DOCUMENT NUMBER: 45:13892
 ORIGINAL REFERENCE NO.: 45:2487i,2488a-e
 TITLE: 3,4-Dihydro-1,3,2H-benzoxazines. Reaction of polyhydroxybenzenes with N-methylolamines
 AUTHOR(S): Burke, W. J.; Weatherbee, Carl
 CORPORATE SOURCE: Univ. of Utah, Salt Lake City
 SOURCE: Journal of the American Chemical Society (1950), 72, 4691-4
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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GI For diagram(s), see printed CA issue.
AB A large number of thiazolidine (I) derivs. were prepared as model compds. to study their stability in solution, cleavage by mercuric and other salts, electrometric and polarographic behavior, etc. The compds. were prepared by: (1) condensation of penicillamine (II) or its esters with aldehydes, (2) condensation of their acetalal, or Schiff bases or ketones; (3) condensation of the Et ester of II with MeCSNH₂ and reduction of the 4-carbomethoxy-2,5,5-trimethylthiazolidine (III) obtained with Al-Hg in moist ether; (4) addition of Me₂C=CO to derivs. of 2-thiazolidine, followed by hydrolysis to yield 2,3-disubstituted derivs. of I; (5) the reaction of β-mercapto-α-amino acids with 4-alkoxy- or 4-(hydroxymethylene)oxazolones under conditions such that concomitant opening of the oxazolone ring occurred to give I. Azothiazolidines: An attempt was made to synthesize α-amino-4-carboxy-5,5-dimethyl-2-thiazolidineacetic acid (IV) as a possible route to the penicillilic acids or the penicillins. The 1st method consisted in coupling diazotized p-ClC₆H₄NH₂ with OHCCNAC₂OEt to p-ClC₆H₄N₂CH(CH₃)CO₂Et (V) and coupling V with DL-II.HCl to the azo ester (VI), S.CMe₂.CH(CO₂H).NH.CICH₃(CO₂Et):N.C₆H₄Cl. Chemical methods of reduction (Zn dust in AcOH and alkaline Na hyposulfite) were resorted to, for no success was achieved by hydrogenation with various catalysts. Expts. in which the product from these chemical redns. was freed from p-ClC₆H₄NH₂, phenylthioacetylated, and then submitted to azlactonization (shaking with Ag₂O in ether), yielded materials devoid of penicillin activity. As an alternative route to compds. of type IV, EtOCH₂C(NO₂)CO₂Me (VII) was prepared. II plus VII did not give a derivative of I. Attempted conversion of imidazolidines to thiazolidines. In order to determine whether the proposed conversion of imidazolidines to I could be realized, II.HCl and 2-[(carboxymethyl-4-carboxyphenylazo)methyl]-1,3-dibenzylimidazolidine (VIII) were refluxed in aqueous MeOH, giving 2-[(carboxymethyl-4-carboxyphenylazo)methyl]-5,5-di-methyl-4-thiazolidinecarboxylic acid. A similar exchange reaction with ethanolamine gave the corresponding oxazolidine. The latter could be converted to derivs. of I by treatment with II.HCl. Some properties of thiazolidines: I derivs. undergo N-substitutions with the usual acylating reagents, such as ClCOCH₂Ph, ketenes, etc. N-Alkylation can be effected with MeI and Na in liquid NH₃. Many I compds. are cleaved by excess Na in liquid NH₃ to N-alkylated cysteines or penicillamines. Desulfurization of I by Raney Ni proceeded easily in aqueous NaHCO₃. Stability of thiazolidines: A number of derivs. of I, RR'C.S.CMe₂.CH(CO₂H).NR'' (IX), were examined for comparison with penicillin and its derivs. Where R and R' = Me and R'' = H, a deep blue FeCl₃ color immediately formed upon boiling an aqueous solution, indicating hydrolysis to a thiol compound. Where R and R' = H and R'' = Et, hydrolysis occurred only after boiling 1-2 min., while when R = R', and R'' = H, no hydrolysis occurred even after 3 h. A series of several thiazolidines were compared with reference to HCHO and BzH. The principal result was that, as a class, 2-alkyl-4-carboxylic acid derivs. of I were stable to both of the aldehydes, while 2,2-dialkyl-4-carboxylic acids were readily decomposed. Oxidation studies on thiazolidines: Thiazolidines containing a free NH group were oxidized by Na metaperiodate with rupture of the ring, followed by oxidation of the liberated mercaptoamino at the thiol group. The 3-acetylthiazolidines, in which the thiazolidine ring is more stable, were

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6-phenyl-1,3,5,5-tetramethyl-2,4-piperidinedione, m. 136-7°; XVI Me ester, m. 137-8°; D-2-(1-carboxyisopropyl)-3-isobutyryl 4-carbomethoxy-5,5-dimethylthiazolidine, m. 147-9°; 6,1,2',3'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-6-phenyl-3,3,5,5-tetramethyl-2,4-piperidinedione, m. 154°; L-isomer, m. 99-102°; 3-acetyl-4-carbomethoxy-5,5-dimethylthiazolidine, yellow oil, m. phenylpenicilloate, b.p. 120°, phenylpenicilloic acid-HCl, m. 220°; DL-2-[(benzamidobenzylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 205°, with softening from 190° penicillamine; DL-2-[(α-phenylacetamido) (1-carbomethoxy-2-mercapto-2,2-dimethylthiazolidine)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 212-13°; D-2-[(α-phenylacetamido) (phenethylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine, m. 175-6°; D-2-[(α-phenylacetamido)benzylcarbamylmethyl]-4-benzylcarbamyl-5,5-dimethylthiazolidine, m. 186-8°; DL-2-[(α-phenylacetamido) carbomethoxymethyl]-4-carboxythiazolidine, m. 155-56°; L-form, m. 160-1°; DL-2-[(α-phenylacetamido) carbomethoxymethyl]-4-carboxythiazolidine, m. 188°; L-2-[(α-phenylacetamido) carbobenzylloxymethyl]-4-carboxythiazolidine, m. 160-2°; D-heptylpenicilloic acid-HCl, m. 190-1°; D-2-[(α-cyclohexylacetamido) carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 182-3°; D-2-[(benzamidobenzylcarbamyl)methyl]-4-carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 190°; DL-2-[(α-phenylacetamido) carbomethoxymethyl]-3-formyl-4-carboxy-5,5-dimethylthiazolidine, m. 175°; D-2-[(α-phenylacetamido) carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 159-60°; α-Et D-benzylpenicilloate, m. 150° (decompn.); benzylamine salt of α-benzyl D-benzylpenicilloate, m. 163-4°; L-2-[(α-(p-acetoxypheyl)acetamido) carbomethoxymethyl]-4-carboxythiazolidine, m. 55-60°; L-2-[(α-(p-methoxyphenyl)acetamido) carbomethoxymethyl]-4-carboxythiazolidine, m. 165-6°; D-2-[(α-(p-methoxyphenyl)acetamido) carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, white powder; 2-[(p-chlorophenylazo) carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 152°; Me (ethoxymethylene)nitroacetate, b.p. 156-7°; Me (anilinoethylene)nitroacetate, m. 109-9.5°; p-(chlorophenylazo)-formylacetic acid, m. 104-5°; 2-[(p-chlorophenylazo)-carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 165-6° (pyridine salt, m. 149°); Et β,β-diethoxy-α-(p-chlorophenylazo)propionate, m. 54-5°; DL-2-α-(2-hydroxynaphthyl)-4-carboxy-5,5-dimethylthiazolidine, m. 129-30°; DL-2-(3-methoxy-4-hydroxynaphthyl)-4-carboxy-5,5-dimethylthiazolidine, m. 184° (decompn.); DL-2-(2-hydroxyphenyl)-4-carboxy-5,5-dimethylthiazolidine, m. 180-1°; DL-2-[(p-chlorophenylazo) carbomethoxymethyl]-4-carboxy-3,5,5-trimethylthiazolidine, m. 182°; 2-[(p-chlorophenylazo) carbomethoxymethyl]-1,3-dibenzylimidazolidine, m. 88-9°; 2-[(p-chlorophenylazo) carbomethoxymethyl]-4-carboxy-5,5-dimethylthiazolidine, m. 150°; 2-[(p-chlorophenylazo) carbomethoxymethyl]-1,3-dibenzyl-4-imidazolidinecarboxylic acid, m. 137°; 2-styryl-1,3-dibenzylimidazolidine, m. 117°; 2-propenyl analog, m. 85-6°; 2-phenyl-4-(4-morpholinylmethylene)-5(4H)-oxazolone, m. 167°; 2-phenyl-5,5-dimethyl-4-thiazolidinecarboxylic acid, m. 141-2°; 2-[(p-chlorophenylazo) carbomethoxymethyl]-5,5-dimethyl-4-thiazolidinecarboxylic acid, m. 151-2°; 2-(formamidocarbomethoxymethyl)oxazolidine, m. 123.5-4.5°; 2-[(p-chlorophenylazo) carbomethoxymethyl]-oxazolidine, m. 145-6°; L-4-carboxy-2,2,3,5,5-pentamethylthiazolidine-HCl, m. 220-1°

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simply oxidized to the corresponding sulfoxides. Reaction of some thiazolidines with CS₂ or COCl₂: S.CMe₂.CH(CO₂Me).NH.CHCNHNH₂ (X) with CS₂ gave S.CMe₂.CH(CO₂Me).N.CH.CH₂.NH.CS (XI) and S.CMe₂.CH(CO₂Me).N.CH.CH₂.S.C.NH (XII). With COCl₂ in the presence of NaHCO₃, X gave only S.CMe₂.CH(CO₂Me).N.CH.CH₂.NH.CO (XIII). 3-(2-hydroxythiazolidine)thiazolidines: Thiazolidines containing a free NH group with ethylene oxide in the presence of BF₃ gave 3-(2-hydroxyethyl) derivs. In the case of isopropylidenebenzylpenicillamine the product isolated was the lactone, Me₂C.S.CMe₂.CH.NH.CH₂.O.CO (XIV). No reaction was obsd. between Me benzylpenicillin and ethylene oxide. Misc. phenylpenicilloic and penicilloic derivs. and some N-alkyl and N-aralkyl compds.: Formylation of Et hippurate afforded Et formylhippurate and Et hippurylhippurate. The di-Et acetal of the former was more satisfactory for condensation with II, giving α-Et phenylpenicilloate, which hydrolyzed to phenylpenicilloic acid. The latter was, however, readily decarboxylated to phenylpenicilloic acid and with Ac₂O gave no evidence of dehydration, but rather of acetylation, and no significant biol. activity was produced. A no. of other syntheses were initiated in the hope of synthesizing a N-Me or N-benzyl analog of "tricyclic penicillin," S.CMe₂.CH(CO₂H).N.CH.CH.NH.CR.O.CO (XV) since some of the reactions could equally well have given the corresponding analogs of the β-lactam formula. Exptl.: An example of each general procedure for prepn. of derivs. of I will be given. (1) Cystine Et ester-HCl was refluxed in abs. EtOH contg. a trace of HCl with a slight excess of paraformaldehyde, 4-carboxythiazolidine-HCl, m. 144-5°, crystd. on addn. of ether to a warm EtOH soln. (2) DL-II Et ester-HCl (1.5 g.) and 0.6 g. MeCSNH₂ were finely ground and heated 30 min. at 100°, then 2-5 h. at 120° (H₂S was evolved and NH₄Cl sepd.), the melt extd. with ether (3 + 15 cc.), and the dried ext. concd. and treated with dry HCl-Et₂O, giving 4-carboxy-2,5,5-trimethyl-2-thiazolidine-HCl, small rods from CHCl₃-ether, subliming at 80-90° (14 mm.) in long white deliquescent needles, m. 140-1°. The free base (350 mg.), b.p. 60-3°, in 80 cc. ether was treated with 2.5 g. amalgamated Al, 8 cc. water added in portions over 3 days, the ether evapd., the oil dried over P₂O₅, dissolved in dry ether, and treated with dry HCl, giving 250 mg. 4-carboxy-2,5,5-trimethylthiazolidine-HCl, m. 113-14° (from CHCl₃-ether). (3) Me₂C=CO (10.5 g.) and 7.6 g. 2-methyl-2-thiazoline in 100 cc. cold EtOAc were stoppered under N, left for 3 days, the soln. extd. with aq. NaHCO₃, washed, dried, and evapd., the residue dissolved in 50 cc. light petroleum, filtered, concd. to a light yellow oil (23 g.), the light pet. removed, the residue in 50 cc. EtOAc, 15 cc. water, and 2 cc. AcOH, acidic materials extd. with aq. NaHCO₃, and the ext. washed and acidified, giving an oil which crystd. on cooling and scratching; recrystn. from aq. MeOH gave 2-methyl-2-(1-carboxyisopropyl)-3-isobutyrylthiazolidine, m. 130-5°. (4) Cystine Me ester-HCl (1.71 g.) and 2.1 g. 2-benzyl-4-methoxymethylene-5(4H)-oxazolone heated in 50 cc. pyridine on the steam bath for 10 min., the pyridine evapd., the residue dissolved in CHCl₃, and the ext. washed with water, and evapd. gave 2-[(α-1,1-phenylacetamido) carbomethoxymethyl]-4-carboxy-1,3-isobutyrylthiazolidine, m. 122°; 2-phenyl-2-(1-carboxyisopropyl)-3-isobutyrylthiazolidine (XVI), m. 157.5-58°; 6,1,2',3'-thiazolidino-

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(decompn.); N-acetyl-N-benzylalanine, m. 103-5°; Me [2-(α-phenylacetamido)-2-carboxyphenylcarbamyl]-β,β-dimethylpropionate, m. 142°; L-α-methylpenicillamine, m. 208-10° (HCl salt, m. 80-120°); L-4-carboxy-3,5,5-trimethylthiazolidine-HCl, m. 191-2°; L-3-methyl-4-carboxythiazolidine-HCl, m. 180-1°; L-α-methylpenicillamine-HCl, m. 160-70° (decompn.); L-N-isopropylcysteine-HCl, hygroscopic; α-Me N4-methyl-L-benzylpenicilloate, m. 165-7.5° (decompn.) [for numbering, see formula (XVIa) below]; L-2-[(α-phenylacetamido)-carbomethoxymethyl]-3-methyl-4-carboxythiazolidine, m. 180° (decompn.); benzylamine salt of α-Et N4-methyl-L-benzylpenicilloate, m. 80-3°; 2-phenyl-4-carboxythiazolidine, m. 158°; 2-phenyl-4-carboxy-5,5-dimethylthiazolidine, m. 152-3°; 2-phenyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine sulfoxide, m. 136° (decompn.); sulfone, m. 207-8° (decompn.); 2-phenyl-3-acetyl-4-carboxythiazolidine sulfoxide, m. 130-2°; sulfone, m. 198-200°; DL-3-chloroacetyl-4-carboxythiazolidine-5,5-dimethylthiazolidine sulfone, m. 110-11°; D-2-isopropyl-3-benzoyl-4-carboxythiazolidine-5,5-dimethylthiazolidine sulfone, m. 119-20°; D-2-phenyl-3-benzoyl-4-carboxythiazolidine-5,5-dimethylthiazolidine sulfone, m. 200°; 2,2-diethoxyethyl isothiocyanate, b.p. 63-5° (phenylthiourea deriv., m. 96°); benzylthiourea deriv., m. 60°; treatment of the isothiocyanate with 2,4-(O₂N)C₆H₃NHNH₂ gave 2,4-(O₂N)C₆H₃NHNH₂:CHCH₂NHCSNH₂CH₂(NO₂)₂, m. 250-2°; 3-(2,2-diethoxyethyl)-5-isopropylidene-2-thiohydantoin, m. 97-8° (2,4-dinitrophenylhydrazine, m. 230-2°); Et α-(3-phenylthiourea)-β-mercapto-β,β-dimethylpropionate, m. 81°; 3-phenyl-5-(1-mercaptisopropyl)-2-thiohydantoin, m. 165° (decompn.); 5-isopropylidene analog, m. 254-7°; 2-carboxythiazolidine-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 149-50° (decompn.); 1,5,3',4'-(2'-carbomethoxymethyl-5',5'-dimethylthiazolidino)-3-phenyl-2-thiohydantoin, m. 123°; 6,1,2',3'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-3-phenyl-5,6-dihydro-2-thiouracil, m. 215-17°; 2-amino-2-methyl-4-carboxythiazolidine-5,5-dimethylthiazolidine, b.p. 104-5°; 4,3,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-2-imidazolidine, m. 124-5°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-2-iminothiazolidine, m. 187-8°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-2-iminothiazolidine, m. 117-18°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-2-iminothiazolidine, m. 197-8°; 3,4,3',2'-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-2-imino-5-carboxythiazolidine, m. 219°; 3-methyl-2-(4'-carbomethoxy-5',5'-dimethylthiazolidino)-5-carboxythiazolidine-2-imidazolidine, m. 162°; 2-methylaminomethyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 207-8°; the lactone of 3-(2-hydroxyethyl)-4-carboxy-2,2,5,5-tetramethylthiazolidine, m. 102°; N-(2-hydroxyethyl)-penicillamine-HCl, m. 148° [free base, m. 174° (decompn.)]; 3-(2-hydroxyethyl)-4-carboxythiazolidine-2,2,5,5-tetramethylthiazolidine, m. 48-9° (lactone, m. 100°); 2-phenyl-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 128° (lactone, m. 104-5°); 2-[(caproylamino) carbomethoxymethyl]-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 127-8° (lactone, m. 132-3°); α-Et N4-methylpenicilloate-HCl, m. 125-7°; α-Et N4-(2-hydroxyethyl)benzylpenicilloate, m. 139-40° (lactone, m. 153-4°); lactone of 2-(α-phenylacetamido)-methyl-3-(2-hydroxyethyl)-4-carboxy-5,5-dimethylthiazolidine, m. 166°; the butanolate of N4-(2-hydroxyethyl)benzylpenicilloic acid, m. 117-18°; lactone of

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 N-(2-hydroxyethyl)benzylpenicilloic acid, m. 175°;
 bis(benzylammonium) salt of N4-(2-hydroxyethyl)benzylpenicilloic acid, m.
 131-2°; benzylammonium salt of the corresponding lactone, m.
 255-7°; N-benzyl- α -phenylacetamide, m. 116-17°; the
 hydrazinium salt of N4-(2-hydroxyethyl)benzylpenicilloic acid
 α -hydrazide, m. 163-4°; N4-(2-hydroxyethyl)benzylpenicilloic
 acid dihydrazide, m. 205° (decomp.); lactone of the
 α -benzylamide of N4-(2-hydroxyethyl)benzylpenicilloic acid, m.
 200-2°; Et hippurylhippurate, m. 128-9°; Et formylhippurate
 2,4-dinitrophenylhydrazones, m. 175-6°; Et formylhippurate di-Et
 acetal, b0.1 150-3°; α -Et phenylpenicilloate-HCl, decomp.
 at 105°; phenylpenicilloic acid, m. 96-7°; N-
 acetylphenylpenicilloic acid, m. 190-1° (decomp.). N-Alkyl and
 N-alkylthiazolidines: 2-(Methylamino)-carbomethoxymethyl-4-carboxy-5,5-
 dimethylthiazolidine-HCl, hygroscopic, amorphous solid; Me-
 methylphenylpenicillate, m. 144-6°; treatment with aniline
 gave the anil, m. 204-5°; Et N-methylhippurate
 b0.1 118°, m. 33-5°; N-methylhippuric
 acid, m. 104-5°; Et N-methylphenylpenicillate,
 m. 129-30°; anil, m. 179°; benzylamine, m. 154°;
 N-benzyl-N-formylglycine Et ester, b0.05 128-32°; Et
 α -(N-formylbenzylamino)- β -hydroxyacrylate, m. 89°; enol
 benzoate, m. 60°; enol acetate, m. 74°;
 N-benzyl- β , β -diethoxyalanine, m. 167-8°;
 N-benzylbenzylpenicillidic acid di-Et acetal, m. 103-4°; Et
 N-benzylhippurate, m. 58-60°; N-benzylhippuric
 acid, m. 109-10°; Et
 N-benzylphenylpenicillate, m. 136-5-7.5°; anil, m. 117-18°;
 benzylamine deriv., m. 117-18°; Et α -(N-benzylbenzamido)-
 β -(carbomethoxymethylamino)-acrylate, m. 180-1°; Et
 N-benzyl-N-caproyllycine, b0.08 132-4°; Et α -(N-
 benzylcaproylamino)- β -benzylaminoacrylate, b0.001 125-35°;
 benzylamine deriv., m. 75°; Et N-methylacetate, b0.01
 80-4°; Et N-methylmethylpenicillate, m. 45-7°; anil, m.
 141°; benzylamine, m. 107-8°; N-benzyl-N-2-hexenoyllycine
 Et ester, b0.5 150°; N-benzyl-N-3-hexenoyllycine Et ester, b0.2
 142-4°; N-benzyl-3-(1-butenyl)-2,4-pyrrrolidinedione, m.
 114-15°; Et N7-benzyl-DL-amylpenicilloate, viscous gum; treatment
 with dry HCl in dry ether gave DL-2-(N-benzylcaproylamino)carbomethoxymethyl
 1)-4-carboxy-5,5-dimethylthiazolidine-HCl, m. 63-71°; Et
 N7-benzyl-DL-amylpenicilloate, glassy solid, m. 50-5° (HCl salt,
 m. 75-84°); benzylamine salt of D-2-(N-benzyl- α -
 phenylacetamido)-carbomethoxymethyl-4-carboxy-5,5-dimethylthiazolidine,
 m. 154-6°; D-2-[(N-methylbenzamido)carbomethoxymethyl]-4-carboxy-
 5,5-dimethylthiazolidine, m. 157-7.5°, [α]D 28.2° (c
 0.8, MeOH); di-Me ester, prep. with CH2N2, b0.001 110-40°;
 [a]D 28.28° (c 0.8, CHCl3); another form of the di-Me ester,
 m. 115-17°, was prep. from D-penicillamine Me ester and Me
 N-methylphenylpenicillate, m. 145-6°; D-2-[(N-methylbenzamido)carbomethoxymethyl]-4-
 carbomethoxy-5,5-dimethylthiazolidine, [a]D 30.2° (c 0.7,
 MeOH); D-2-[(N-methylbenzamido)carbomethoxymethyl]-4-carboxy-5,5-
 dimethylthiazolidine, m. 152-3°, [a]546125 29.8° (c
 1.274, alc.); N-benzylhippuric hydrazide, m. 85-6°;
 4-(N-methylbenzamido)-5-pyrazolone, m. 237-40°, with slight softening
 at 225°; α -[isopropylidene(carbomethoxy)methylamino]methylene
 α -(N-methylbenzamido)glycine Et ester,
 Me2C(CO2Me)NHCH2C(NMeBz)CO2Et, m. 146°; α -Et
 N4-acetyl-N7-methyl-D-phenylpenicilloate (XVIa), m. 156-7°;
 [a]546125 127.5° (c 1.2, alc.); N4-isobutyryl homolog, m.

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 ester of DL-penicillamine acid, m. 215-19°; D-2-isopropyl-3-
 benzoyl-4-carboxy-5,5-dimethylthiazolidine, m. 163-4° (Me ester,
 prep. with CH2N2); 2-phenyl-4-carbomethoxythiazolidine, b0.5-1
 153-5°, nD20 1.5738; L-2-phenyl-3-acetyl-4-carboxythiazolidine, m.
 152-5-4°; 2-phenyl-3-benzoyl-4-carboxythiazolidine, m.
 153-4°; 2-phenyl-3-phenylacetyl-4-carboxythiazolidine, m.
 171-3°; DL-2-isobutyl-4-carboxy-5,5-dimethylthiazolidine, m.
 145-7°; L-2-(α -hydroxyphenyl)-4-carboxythiazolidine, m.
 167° (decomp.); L-2-hexyl-4-carboxythiazolidine, m. 148-50°
 (decomp.); DL-2-phenyl-4-carboxythiazolidine, m. 165-70°;
 [a]D 21-30.5° (c 1.0, N HCl); L-2-benzyl-3-carbomethoxy-4-
 carbomethoxythiazolidine, m. 135°; 2-spirocyclohexyl-4-carboxy-
 5,5-dimethylthiazolidine, m. 200-1°; DL-2-spirocyclohexyl-4-
 carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 183°;
 L-2-hexyl-4-carboxy-5,5-dimethylthiazolidine, m. 113-14°;
 DL-isomer, m. 120-1°; DL-2-hexyl-3-acetyl-4-carboxy-5,5-
 dimethylthiazolidine, m. 139-40°; DL-2-phenyl-4-carboxy-5,5-
 dimethylthiazolidine, m. 145-6°; HCl salt, m. 172-3°;
 (decomp.); DL-2-phenyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m.
 154°; DL-2-phenyl-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m.
 196-7°; DL-2-phenyl-3-carbomethoxy-4-carboxy-5,5-
 dimethylthiazolidine, m. 145-9°; DL-2-phenyl-3-benzylcarbonyl-4-
 carbomethoxy-5,5-dimethylthiazolidine, m. 199-203°;
 D-2-(p-chlorophenyl)-4-carboxy-5,5-dimethylthiazolidine, isolated as the
 semicryst. Na salt; DL-2-(α -hydroxyphenyl)-4-carboxy-5,5-
 dimethylthiazolidine, m. 190-1° (decomp.); DL-2-benzyl-4-carboxy-
 5,5-dimethylthiazolidine, m. 108-10°; DL-II and 2,3-hexanedione
 gave a product isolated as the HCl salt, m. 161-2° (decomp.);
 DL-2-spirocyclohexyl-4-carboxy-5,5-dimethylthiazolidine-HCl, m.
 219° (decomp.). No satisfactory thiazolidines were prep. from
 MeOPH, Ph2CO, MeCHClCOMe, 3,4-dihydro-1(2H)-Naphthalenone, glucose,
 benzoin, quinone, Et cyclohexan-1-one-2-carboxylate, Et aminoacetate,
 MeCH:CHCHO, and CH2:CHCHO; D-2-(α -camphoryl)-4-carboxy-5,5-
 dimethylthiazolidine, m. 175°; L-2-diethoxymethyl-4-
 carbomethoxythiazolidine, m. 149° (decomp.); DL-2-diethoxymethyl-4-
 carbomethoxy-5,5-dimethylthiazolidine-HCl, m. 99-101° (another fraction
 of the same compn. m. 126-7°); DL-2-(3-methoxy-4-acetoxypheyl)-3-
 acetyl-4-carboxy-5,5-dimethylthiazolidine, m. 199°;
 DL-2-(α -acetoxypheyl)-3-acetyl-4-carboxy-5,5-dimethylthiazolidine, m.
 203-4°. Dicarboxythiazolidine derivs.: L-2,4-Dicarboxy, m.
 184-5°; D-2-carboxybutyryl-4-carboxy-5,5-dimethyl, m. 141-2°;
 D-2-carboxy-4-carboxy-5,5-dimethyl, isolated as the Ba salt
 (benzylamine salt, m. 156-7°); D-2-carboxy-3-nitroso-4-carboxy-
 5,5-dimethyl, m. 167-9° (benzylamine salt, m. 152-3°);
 D-2-carboxybutyryl-3-nitroso-4-carboxy-5,5-dimethyl, isolated as the
 benzylamine salt, m. 134-5°; L-2-carboxybutyryl-4-carboxy-
 b0.1 115-17°; DL-2,4-dicarboxy-2,5,5-trimethyl, m. 174°
 (decomp.); L-2-methyl-2-carboxybutyryl-4-carboxy-5,5-dimethyl, b0.55
 118-21°, nD20 1.4952; D-2-carboxybutyryl-4-carboxy-5,5-dimethyl,
 m. 152-4°, [a]D 23 122.5° (c 0.392, MeOH) (HCl salt, m.
 128-38°); D-2-carboxybutyryl-4-carboxy-5,5-dimethyl (HCl
 salt, m. 167-9°); [a]D 23 78° (c 0.94, MeOH);
 D-2-carboxybutyryl-4-carboxy-5,5-dimethyl, m. 100-5°;
 D-2-carboxybutyryl-4-carboxy-5,5-dimethyl (HCl salt, m.
 147-9°); D-2-carboxybutyryl-3-methoxyl-4-carboxy-5,5-dimethyl,
 m. 128-30°; D-2-carboxybutyryl-3,4-dicarboxy-5,5-dimethyl,
 b0.5 160°; L-2-cyanomethyl-3-acetyl-4-carboxy-5,5-dimethyl,
 m. 112-13°; D-2-carboxybutyryl-4-carboxy-5,5-dimethyl, m.
 114-15° (decomp.); D-2-carboxybutyryl-4-carboxy-2,5,5-trimethyl,

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 197°, [a]546123 60.4° (c 0.612, EtOH); α -Et
 β -Me N4-isobutyryl-N7-methyl-D-phenylpenicilloate, m. 97°;
 [a]5461 28° (c 0.5, EtOH); α -Et N4-benzoyl-N7-methyl-D-
 phenylpenicilloate, m. 224°. Alkyl and aryl thiazolidines:
 2-Spirocyclohexyl, m. 165-8°; 2-Ph, m. 105-9°;
 2-(α -methoxyphenyl), m. 94-6°. Monocarboxythiazolidine derivs.:
 L-2-Methyl-4-carboxy, m. 162-3° (Et ester-HCl, m. 123-4°);
 4-carboxy-5-Me, m. 208-9° (decomp.) [from "B" thiothreonine
 (Carter, et al., C.A. 35, 5463.3, a 2nd isomer, from "A" thiothreonine, m.
 193-4°, was obtained)]; 2,2-dimethyl-4-carboxy, b0.5
 58-60.5°; L-2,2-dimethyl-3-carbomethoxy-4-carboxy, isolated as the
 benzylamine salt, m. 124-8°; D-4-carboxy-5,5-dimethyl, m.
 196-7° (decomp.); L-isomer, m. 193-4°; DL-mixt., m.
 200-1° (decomp.) (HCl salt, m. 199-200° or 191-2°
 (decomp.), according to another group of workers); 3-acetyl-4-carboxy-5,5-
 dimethyl, m. 152-5° (Me ester, yellow sirup); 3-chloroacetyl-4-
 carboxy-5,5-dimethyl, m. 133-5°; DL-3-benzoyl-4-carboxy-5,5-
 dimethyl, m. 151-2° (Me ester, m. 63-4°, converted by KMnO4
 to a sulfone, m. 133-4°); D-3-carbomethoxy-4-carboxy-5,5-
 dimethyl, isolated as the benzylamine salt, m. 140-1°;
 DL-3-phenylcarbonyl-4-carboxy-5,5-dimethyl, m. 191-2°;
 3-[(carbomethoxymethyl)carbonyl]-4-carboxy-5,5-dimethyl, m.
 80-2°; D-2-cyanomethyl-4-carboxy-5,5-dimethyl, m. 184-5°
 (decomp.); Me ester-HCl, m. 170-1°; [a]D 97° [free
 base, m. 78-9°, [a]D 101° (c 1.0, MeOH)];
 4-carboxy-2,5,5-trimethyl, m. 103-5°; 2-isopropyl-4-carboxy, m.
 181° (decomp.); 2-methyl-2-ethyl-4-carboxy, m. 132-3°
 (decomp.) (HCl salt, m. 145-6°); 2-isopropyl-3-carbomethoxy-4-
 carboxy, m. 88.5-90° (benzylamine salt, m. 149-9.5°);
 2-isopropyl-3-carboxy-4-carboxy, m. 63.5-4.5° (benzylamine salt,
 m. 113.5-14.5°); 2-isopropyl-3-carbomethoxy-4-carboxy, oil;
 L-2-acetyl-4-carboxy, m. 155° (decomp.); L-2-isobutyl-4-carboxy,
 m. 154° (decomp.); 2-ethyl-4-carboxy-5,5-dimethyl, m.
 173-4°; 2-ethyl-3-acetyl-4-carboxy-5,5-dimethyl, m. 152-4°;
 DL-2-(1,2-dihydroxyethyl)-4-carboxy-5,5-dimethyl, m. 201°
 (decomp.); DL-4-carboxy-2,2,5,5-tetramethyl, m. 48-9° (HCl
 salt, m. 162-3°; picrate, m. 150°); D-isomer, b0.1
 59°, m. 18-20°, [a]546125 116° (c 1.5, alc.)
 (HCl salt, m. 143-4°), [a]546127 91° (c 0.93, water));
 DL-4-carboxy-2,2,5,5-tetramethyl, b0.05 42-5° (HCl salt, m.
 167-8°). The following esters of DL-2,2,5,5-tetramethyl-4-
 thiazolidinecarboxylic acid (XVII) were also prep.: Pr (HCl salt, m.
 160-1°; picrate, m. 137-9°); iso-Pr (HCl salt, m.
 169-70°; picrate, m. 149-50°); Bu, b0.1 80° (HCl
 salt, m. 160°; picrate, m. 132°); iso-Bu (HCl salt, m.
 170°; picrate, m. 146-7°); Am (HCl salt, m. about
 110°); iso-Am (HCl salt, m. 155-6°); hexyl (HCl salt, m.
 128°; picrate, m. 138°); isohexyl (HCl salt, m. 163°);
 picrate, m. 130°; Deriv. of XVII: 130°; 3-formyl, m. 141-2°
 (Me ester, b0.1 110-15°); 3-Ac (Me ester, m. 57-8°);
 3-chloroacetyl, m. 148-9° (decomp.); 3-Bz (Me ester, m.
 88-9°); 3-phenylacetyl, m. 159-60°; L-2-Methyl-2-acetyl-4-
 carbomethoxythiazolidine, m. 160° (decomp.); however, as subsequent
 tests and UV data were more in agreement with an open thiol structure, the
 constitution of this product is doubtful. DL-4-Carboxy-2,2,5-trimethyl-5-
 ethylthiazolidine-HCl, m. 209-10° (decomp.); DL-2-ethyl-4-carboxy-
 2,5,5-trimethylthiazolidine, m. 183-3.5° (decomp.);
 DL-2-propyl-4-carboxy-5,5-dimethylthiazolidine, m. 97-9°;
 DL-2-iso-Pr isomer, m. 181-2.5° (the Me ester with H2O2 gave the Me

L7 ANSWER 41 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 ester, m. 153-4°; DL-isomer, m. 176-7°; DL-2-carbamylmethyl-4-
 carbomethoxy-2,5,5-trimethyl, m. 199-200°; L-2-(phenylcarbomethoxymethyl)-
 4-carboxy, m. 163-4°; L-2-(phenylcarbomethoxymethyl)-4-carboxy, m.
 165°; L-2-(phenylcarbomethoxymethyl)-4-carboxy, m. 60-1°;
 L-2-(phenylcarbomethoxymethyl)-4-carboxy, m. 57-8° (HCl salt, m.
 125-6°); L-2-(phenylcyanomethyl)-4-carboxy, m. 159-60°
 (decomp.) (Et ester-HCl). Amino monocarboxythiazolidine derivs.:
 L-2-Aminomethyl-4-carboxy (di-HCl salt, m. 145-6°);
 L-2-(benzylaminomethyl)-4-carboxy, m. 208-10° (decomp.);
 L-2-(carboxyamino)thiazolidine-4-carboxy, m. 159°;
 L-2-(carboxyamino)thiazolidine-3-phenylacetyl-4-carboxy, m. 198°
 (decomp.); DL-2-aminomethyl-4-carboxy-5,5-dimethyl (di-HCl salt, m.
 161-2°); DL-2-aminomethyl-4-carboxy-5,5-dimethyl, m. 200°
 [di-HCl salt, m. 200-1° (decomp.)]; DL-2-aminomethyl-4-carboxy-
 5,5-dimethyl (picrate, m. 169-70°); [di-HCl salt, m. 167-8°
 (decomp.)]; DL-2-(carboxyamino)thiazolidine-4-carboxy-5,5-dimethyl (HCl
 salt, m. 183°); 2-(benzamidocarbomethoxymethyl), m. 108-11°;
 2-(benzamidocarbomethoxymethyl)-3-isobutyryl, m. 201°; 2-[(α -phen-
 ylacetamido)-carbomethoxymethyl], m. 108-11° (HCl salt, m.
 172-3° (decomp.); DL-2-(p-tolylsulfonamido)thiazolidine-4-carboxy-5,5-
 dimethyl (HCl salt, m. 175° (decomp.)), from DL-II, HCl and
 p-MeC6H4SO2NHCH2CH(OEt)2, m. 67°; the latter gave a
 dicarboxyphenylhydrazones, m. 175°; the thiazolidine deriv. formed a
 Me ester-HCl, m. 188-90° (decomp.). p-ACNHCH4SO2C1 converted
 DL-isopropylidenebenzylamine-HCl to the diketopiperazine, m.
 210-12°; β -MeCH(NH2)CH2CH(OEt)2, m. 113°; was 97-9°;
 converted to β -(caproylamino)butyraldehyde di-Et acetal, b0.025
 150°, nD22 1.4475 (dinitrophenylhydrazones, m. 154°);
 β -(α -phenylacetamido)butyraldehyde di-Et acetal, b0.007
 160-2°, nD22 1.5130 (2,4-dinitrophenylhydrazones, m. 184°);
 DL-2-(2-aminopropyl)-4-carboxy-5,5-dimethylthiazolidine-2HCl, m.
 201° (decomp.); β -(caproylamino)propionaldehyde di-Et acetal,
 b0.07 132° (dinitrophenylhydrazones, m. 154-5°);
 DL-2-(2-caproylamino)thiazolidine-4-carboxy-5,5-dimethylthiazolidine-HCl, m.
 186° (decomp.). Amino dicarboxythiazolidine derivs.:
 L-2-(Formamidocarbomethoxymethyl)-4-carboxy (HCl salt, m. 185°
 (decomp.)); Et ester of the free base, m. 109°;
 D-2-(aminocarbomethoxymethyl)-4-carboxy-5,5-dimethyl, b0.001
 100°, nD24 1.5119; the DL-compd. HCl salt, hygroscopic powder;
 DL-2-(aminocarbomethoxymethyl)-4-carboxy-5,5-dimethyl mono-Ba and mono-Na salts
 were prep.; DL-2-(aminocarbomethoxymethyl)-4-carboxy-5,5-dimethyl (di-HCl
 salt, m. 72-5° (decomp.)); D-2-(aminocarbomethoxymethyl)-4-
 carbomethoxy-5,5-dimethyl, purified by evaporative distn. at 0.003 mm. and
 100°, [a]D 35° (c 0.3, EtOH); D-2-
 (aminocarbomethoxymethyl)-3-phenylacetyl-4-carboxy-5,5-dimethyl (HCl salt,
 m. 118-20°); D-(2-aminocarbomethoxymethyl)-3-phenylacetyl-4-
 carbomethoxy-5,5-dimethyl (HCl salt, m. 151-3°); the corresponding
 dicarboxylic acid HCl salt, m. 156-8°. MeI and
 2-(aminocarbomethoxymethyl)-4-carboxy-5,5-dimethyl refluxed for 20 h.
 gave a red oil. Tricarboxythiazolidine derivs.: D-2,2-Dicarboxy-4-
 carbomethoxy-5,5-dimethyl (HCl salt, m. 151-2° (decomp.));
 DL-2-carboxy-2-carboxybutyryl-4-carboxy-5,5-dimethyl, m.
 148-9°; Thiazolidines with linked and fused heterocyclic
 substituents: 2-(2-Furyl)-DL-4-carboxy-5,5-dimethylthiazolidine, m.
 141-3° (decomp.); 4,3,2',3'-(D-4'-carbomethoxy-5',5'-
 dimethylthiazolidine)-2-imidazolidine, m. 128-9°; DL-compd., m.
 124-5°; 4,3,2',3'-(D-4'-carbomethoxy-5',5'-dimethylthiazolidine)-5-
 carbomethoxy-2-imidazolidine, m. 168-9° (decomp.);
 1-benzyl-2-phenyl-3,4,3',2'-(4'-carbomethoxythiazolidine)imidazolidine, m.

L7 ANSWER 41 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
G1 For diagram(s), see printed CA Issue.
AB 163'; 3,4,3',4'-(2'-benzylthiazolido)-1-phenylhydantoin, m.
91-2'; 3-(carboxymethylcarbonyl)-4-carboxymethoxy-5,5-
dimethylthiazolidine, m. 80-2'; 1-carboxymethyl-3,4,3',4'-(5',5'
dimethylthiazolido)hydantoin, m. 151-2'; Addnl. information in
printed abstr.

ACCESSION NUMBER: 1950:49326 CAPLUS
DOCUMENT NUMBER: 44:49326
ORIGINAL REFERENCE NO.: 44:9427f-i, 9428a-i, 9429a-i, 9430a-i, 9431a-i, 9432a-
i, 9433a-i, 9434a-i, 9435a-c
TITLE: Thiazolidines
AUTHOR(S): Cook, A. H.; Heilbron, I. M.
CORPORATE SOURCE: Imperial Coll. Sci., London
SOURCE: Chemistry of Penicillin (H. T. Clarke, et al.)
(Princeton Univ. Press) (1949) 921-72
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 42 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN

G1 For diagram(s), see printed CA Issue.

AB A series of indole deriva., o-CGH4.CR:CR'.NH (I), related to
gramine, is prepared, by the Mannich reaction. Reduction of
o-OZNCGH4CH2COOCH2, prepared according to DiCarlo (C.A. 38, 5218.1), with
Na2S2O4 gives the indolecarboxylic acid which, refluxed with EtOH, gives
904 Et ester (II), m. 115-20°. Dropwise addition over a period of 2
h. of 24 g. EtCHO to 64 g. Et2NCH2CH2CH2CH(NH2) Me at 0° with
stirring, adding a small amount of KOH, keeping the mixture 1 h., drying the
organic layer over KOH, keeping it overnight in a refrigerator, and
distilling over NaOH give the aldimine, b34-35 124-8°, which,
hydrogenated at 3 atmospheric with 5% Pd-charcoal, gives 684
Et2NCH2CH2CH2CH(NHPr)Me (III), b30-32 128-35°, b. 234-6°
(di-HCl salt, slightly hygroscopic crystals, m. 219.5-20.5°). I
are obtained by treating the appropriate indole derivative in AcOH with a

104 excess of NHR2 and then with 37% HCHO according to the procedure used by
Kuhn and Stein (C.A. 31, 3913.9) for the synthesis of gramine.
The mixture is diluted with H2O, washed with ether, made alkaline, and the
precipitate is
recrystd. In this way the following I are prepared (R, R', yield, and m. p.
in the order given): Me(PhCH2)NCH2, H, 904, 114°; MePhNCH2, H, 74,
126-7°; (CH2:CHCH2)2NCH2.H, 604, 77.5-8°; CH2.(CH2)4.NCH2,
Me, 794, 156-7°; CH2.CH2.O.CH2.CH2.NCH2, Me, 924, 175-6°;
Pr(Et2N(CH2)3CHMe)NCH2, CO2Et, 804, 78-9°; Me(PhCH2)NCH2, CO2Et,
934, 104-5°; CH2.CH2.O.CH2.CH2.NCH2, CO2Et, 944, 152-3°;
(CH2:CHCH2)2NCH2, CO2Et, 884, m. 100-1°; Pr2NCH2, CO2Et, 944,
78-9°; (HOCH2CH2)2NCH2, CO2Et, 704, m. 105-7°; Me2NCH2,
CO2Et, 834, m. 86-7°.

ACCESSION NUMBER: 1950:49315 CAPLUS
DOCUMENT NUMBER: 44:49315
ORIGINAL REFERENCE NO.: 44:9409a-e
TITLE: The preparation of Mannich bases related to
gramine
AUTHOR(S): Brehm, Warren J.; Lindwall, H. G.
CORPORATE SOURCE: New York Univ.
SOURCE: Journal of Organic Chemistry (1950), 15, 685-7
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 43 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN

G1 For diagram(s), see printed CA Issue.
AB cf. C.A. 31, 3888.2. The condensation of CH2O and alkoxyphenylalkylamines
in the presence of acid gave mixts. of low-polymeric bases which could be
partially separated into their constituents. Polymers with 3-4 residues of
the parent amine joined by CH2 groups between the rings had a
pronounced and enduring effect in lowering blood pressure, the presence or
absence of HOCH2 groups (presumably attached to terminal rings) not being
critical. Standard preps.: Slow addition of 5.85 cc. formalin solution to

12.4 g.
4-MeOC6H4CH2CH2NHMe (I) in 15 cc. H2O at 0-5°, then 30 cc. cold
concentrated HCl (final concentration 6 N), and heating on the steam bath x
hrs. gave
GC-142-x; x generally was 4 h., GC-142-4 being more potent than GC-142-1
and -2. A minor variation was Et2O extraction of the mixture before
addition of the
HCl. The solution was then concentrated on the steam bath in vacuo, the
residue
dissolved in 40 cc. absolute EtOH, 1 volume EtOAc added, and the jelly,
formed
by 16 h. cooling, converted by 2 vols. Et2O to a granular precipitate,
which was

filtered rapidly, washed with anhydrous Et2O, and dried in vacuo. Other
preps. were M-25, from 3,4-(MeO)2C6H3CH2CH2NHMe, M-27 from the
2,3-analog, GD-6 from hordenine, M-96 from hordenine Me ether (II), M-118
from 11.MeCl, M-114 from 2-MeOC6H4CH2CH2NHMe2, GC-114 from
4-MeOC6H4CH2NHMe, GC-104-II from o-anisidine, and GC-110, the quaternary
salt prepared by methylation of GC-104-II with MeI in MeOH and Na2CO3.
Isolation of dimers: GC-60 was prepared by addition of 3 cc. formalin and 20
cc. 20% HClO4 in the cold to 6.4 g. I, heating 2 h. in the steam bath,
chilling, and crystallization of the gummy solid twice from H2O to 3.7 g.
colorless microcryst. salt, converted to the base, then to the HCl salt, m.
261-2° (from EtOH-Et2O). The free base was distilled at
0.4 µ and 125-30° bath temperature, giving a product of mol. weight 329
(342 calculated for C21H30N2O2), again converted to the HCl salt, m.
264-5°. GC-55: 3,4-Me(MeO)C6H3CH2CH2NHMe2 (III), CH2O, and HCl gave
a poor yield of impure dimer HCl salt, m. 221-2°, and much higher
polymers. GC-125-I and -II were formed in the attempted preparation of a
trimer; 4 g. formalin, 9.65 g. III, and 48 g. concentrated HCl were treated

2 h.
at 30-40° with a current of HCl gas, the mixture concentrated in vacuo, the
residue (mostly monochloromethyl derivative ?) treated with 5.4 g.
4-MeOC6H4CH2CH2NHMe2 and 10 cc. concentrated HCl 7 h. on the steam bath,
concentrated
in vacuo, and the residue made alkaline in H2O; Et2O extraction gave
GC-125-I,
Et2O-soluble, 520 mol. weight (Rast), and GC-125-II, Et2O-insol. and
EtOAc-soluble

Distillation at 0.3 µ to 130° of 275 mg. GC-114 gave 115 mg.
distillate of mol. weight 244 (314 for dimer) and 140 mg. residue,
496 mol. weight (477 for trimer). The best fractionation of polymers was
with the Craig counter-current distribution method (C.A. 41, 6172a). M-96
was largely freed of dimer (about 25%) by partial basification of the
aqueous
solution and solvent extraction, leaving 70% GC-81-II. Distribution of two
1-g.
portions of this in 9 separatory tubes between 120 cc. each of 50-50
C6H6-hexane and 75% aqueous MeOH in each tube, and conn. gave a total of 1.4
g. residue (IV) in tubes 0-4 and a sep. hydrophilic component (V) in tubes
7-8. IV showed homogeneity on further distribution, and 2 fractions,

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tested as GC-131-2 and -3, were converted to HCl salts, the former giving
no CH4 (Zarewitinoff). V from 3 runs (490 mg.) on redistribution gave 185
mg., GC-132-8, analyzing C37H55N3O5 (trimer with 2 HOCH2 groups), contg. 2
active H atoms (1.12 cc. CH4 found, 1.07 calcd. for mol. wt. of 621).
Distn. of 0.1 g. free base, at 0.2 µ and 175°, gave 40
mg. (mol. wt. 296), 25 mg. at 208° (mol. wt. 572 found, 561 calcd.
for trimer), and 25 mg. residue (557). Terminal fractions (655 mg.) from
several large distributions were redistributed between 50-50 C6H6-hexane
and 55% aq. MeOH, giving in tube 0 135 mg., 746 mol. wt. in camphor (782
calcd. for tetramer with 1 HOCH2 group), and 0.61 cc. CH4 (0.80 cc.
calcd.) (Zarewitinoff). The contents of tube 8 (90 mg.) gave a mol. wt. of
567 in borneol (612 with depression of m.p. in lit. 35.6° against
33° obsd., 621 calcd. for trimer with 2 HOCH2 groups), and 1.57 cc.
CH4 (1.85 calcd.). No active fraction gave cryst. salts and the phys.
properties and anal. data indicated that sepn. had been between types
only, not species. GC-114 and the polymer from 4-MeOC6H4CH2NHMe2 were less
potent and more toxic than others; the 4 dimer was higher and d.p. lower,
anticipated with a cationic group only one stage removed from the C6H6
ring. The high potency of GC-110 in contrast with GC-104 II showed the
dependence of activity on the presence of groups that would be cationic
under physiol. conditions. Expts. on a trimer contg. 2 or 3 properly
spaced cationic groups, which should give strong depressor action, are
under way. Pharmacol. data on the above comds. will be reported
elsewhere. A structure with crosslinking between N atoms by CH2O was
eliminated when M-96 and M-118 both showed max. potency, so CH2 links
between arom. nuclei seem more probable, as shown in VI, Z and Z' being H,
CH2OH, or CH2Cl groups.

ACCESSION NUMBER: 1949:36537 CAPLUS
DOCUMENT NUMBER: 43:36537
ORIGINAL REFERENCE NO.: 43:6593h-i, 6594a-i, 6595a-c
TITLE: A family of long-acting depressors
AUTHOR(S): Baltzly, Richard; Buck, Johannes S.; De Beer, Edwin
J.; Webb, Frederick J.
SOURCE: Journal of the American Chemical Society (1949), 71,
1301-5
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L7 ANSWER 44 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diagram(s), see printed CA issue.
 AB It is proposed that CO(NH₂)₂ reacts with HCHO as an amino acid amide; in such a mol., the amide-NH₂ would react with HCHO to yield a methylenimine derivative which would trimerize to a cyclic trimethylenetriamine compound and the amide-NH₂ would react to yield methylenebisamide links between the rings. The resulting polymer would be a highly cross-linked structure. H₂NCH₂CONH₂·HCl (1 mol) and 2 mol HCHO in aqueous solution at pH 4.2 (NaOH) at room temperature, the H₂O being removed in a desiccator over P₂O₅, give a brittle polymer, C₂₁H₃₆N₁₂O₆, decomps. about 200°; gelation occurs only when 1.5 or 2 mol HCHO are present; the reaction is twice as fast with 1.5 as with 2 mol of HCHO; gelation does not occur in solns. of pH less than 3.2 or of 5 or higher; at 0°, a solution of pH 4.2 gelled during several weeks to yield a very soft, opaque material; at 60° no gelation is observed. The preparation of H₂N(CH₂)₅CO₂Et (I) (52%) from the HCl salt (96% from ε-aminocaproic acid) is described. I (25 g.) and 275 cc. concentrated NH₄OH, shaken for 60 h., give 63% of ε-aminocaproamide (II), m. 50-1°, very hygroscopic and absorbs CO₂ from the air. II (1 mol) and 2 mol aqueous HCHO evolve heat on being mixed; a semisolid gel is formed in about 1 h. and a product resembling "art gum" after 4 days; the yield of the polymer, C₁₅H₂₄N₁₀O₂, decomposing 185°, is 97.5% (based on 1.5 CH₂ units per amide unit); H₂NCH₂CO₂Et (21 g.) and 280 cc. 35% aqueous MeNH₂ shaken for 60 h., the excess MeNH₂ removed at 40°, the H₂O removed by distillation with C₆H₆ at 30°, the residue in 20 cc. H₂O treated with 25 cc. concentrated HCl and 400 cc. absolute EtOH, give 60% of glycine methylamide-HCl (III), m. 153.5-6°. III (1.25 g.) and 0.77 cc. HCHO, made slightly alkaline with NaOH and heated at 60° for 4 h., give 12% of the polymer, (C₄H₈N₂O₃)₃, m. 167.5-9° (purification described). MeNHCH₂CONH₂ (1 mol) and 2 mol HCHO, acidified with 2 drops concentrated HCl, heated at 60° for 4 h., give an amber glass (viscous liquid in air), C₄H₉N₂O₂Cl; this is probably a linear polymer of a low mol. weight. AcNHCONH₂ does not react with HCHO in neutral basic solution; heated in an acid solution at 70° for 4 h., they give a resinous material, m. 245-6° (34.45% N); another preparation m. 275-8.5° (decomposition), 28.74 N. H₂NCO₂Et (89 g.) and 93 cc. HCHO with 25 ml. concentrated HCl, refluxed 5 h., give 95-100% of EtO₂CN·CH₂·N(CO₂Et)₂·CH₂·N(CO₂Et)₂·CH₂·N(CO₂Et)₂; the EtO groups could not be replaced by NH₂ groups.

ACCESSION NUMBER: 1946:37225 CAPLUS
 DOCUMENT NUMBER: 40:37225
 ORIGINAL REFERENCE NO.: 40:7166d-1,7167a
 TITLE: Structure of urea-formaldehyde resins
 AUTHOR(S): Marvel, C. S.; Elliott, J. R.; Boettner, Fred E.; Yuskas, Henry
 CORPORATE SOURCE: Univ. of Illinois, Urbana
 SOURCE: Journal of the American Chemical Society (1946), 68, 1681-6
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 45 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 AB and XVI is proved by oxidn. with KMnO₄ in 10% excess of the calcd. amt. in dry Me₂CO at 0°, with XIV giving 48% 3-phenyl-4(3)-quinazoline, m. 138-9° (picrate m. 177-8°), XV giving 36% 3-p-bromophenyl-4(3)-quinazoline, m. 189-90° (picrate m. 171-3°), and XVI giving 87% 3-p-methoxyphenyl-4(3)-quinazoline, m. 193.5-4°. The latter is synthesized in 28% yield by heating o-NH₂CH₂CO₂H and formyl-p-anisidine at 150° for 1.5 h. When 0.02 mol. 1-naphthol (XIX), 2-naphthol (XX), or carvacrol (XXI) and 0.02 mol. II, III, or VII in 20 cc. abs. EtOH are refluxed for 15-60 min., the following (aminomethyl)phenols are formed: XIX and VII give 77% 2-(1-piperidylmethyl)-1-naphthol, m. 133.5-4.5°, XX and VII give 97% 1-(1-piperidylmethyl)-2-naphthol, m. 95-6.5° (under anhyd. conditions with ligroin (b. 90-120°) as solvent the yield is 61%), XX and II give 80% 1-(p-toluenemethyl)-2-naphthol (XXII), m. 136.5-7°, XX and III give 81% 1-(p-chloroanilinomethyl)-2-naphthol, m. 139-41.5°, and XXI and VII give 24% (1-piperidylmethyl)carvacrol, m. 182-3°. XXII dissolves in 10% NaOH on heating and from the soln. XXII is recovered unchanged on acidification, indicating that its p-(toluenemethyl) group is not attached to the OH group and that its phenolic character is relatively weak. When XX and IX are heated in EtOH in the presence of EtONa, 52% 1,1'-methylenebis-2-naphthol (XXIII), m. 194-5°, is obtained. In the absence of EtONa 59% XXII, 22% XXIII, some unchanged XX and 80% p-MeC₆H₄NH₂·HCl can be isolated. When a mixt. of 0.03 mol. PhNMe₂ and 0.01 mol. VII is satd. with HCl, the solid dissolved in hot abs. EtOH and refluxed for several hrs., 22% bis(p-dimethylaminophenyl)methane, m. 88-90°, is formed. Carbazole (XXIV) and HCHO in hot glacial AcOH or with VII in the presence of Ac₂O give methylenediacetals, m. 301-3°, in 52 and 77% yield, resp. When, however, XXIV and HCHO are refluxed in 85% EtOH in the presence of piperidine, 99% 9-(1-piperidylmethyl)carbazole (XXV), m. 99-9.5°, is obtained. XXV is also formed on heating of a mixt. of 0.02 mol. XXIV with 0.01 mol. VII for 1 h. at 180-5°. The analogy between HOCH₂OH and I is further demonstrated by the formation of (aminomethyl)imides by interaction of phthalimide (XXVI), piperidine and HCHO. On heating of an equimol. mixt. of XXVI, HCHO, and piperidine in 80% EtOH, or on refluxing of a soln. of 0.02 mol. XXVI and 0.02 mol. VII in 20 cc. EtOH for 2 h., N-(1-piperidylmethyl)phthalimide, m. 119-19.5°, is obtained in 95 and 92% yield, resp. Under the same conditions succinimide (XXVII), piperidine and HCHO or XXVII and VII give N-(1-piperidylmethyl)succinimide, m. 107-7.5°, in 46 and 89% yield, resp. Dimethyldihydroresorcinol (XXVIII) used as reagent for aldehydes also reacts with the I. By dissolving 0.01 mol. XXVIII and 0.005 mol. I in 10-15 cc. EtOH or Bu₂O with minimal warming, the following yields of methylenedimethones, m. 188-9°, are obtained from the various I: from II in EtOH 93%, in Bu₂O 97%; from III in EtOH 99-100%, in Bu₂O 96-100%; from IV in Bu₂O 96%; and from V in Bu₂O 58-78%.

ACCESSION NUMBER: 1942:12323 CAPLUS
 DOCUMENT NUMBER: 36:12323
 ORIGINAL REFERENCE NO.: 36:1938b-1,1939a-h
 TITLE: Some reactions of methylenediamines as ammono aldehydes
 AUTHOR(S): Feldman, J. R.; Wagner, E. C.
 SOURCE: Journal of Organic Chemistry (1942), 7, 31-47
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L7 ANSWER 46 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The structural analogy between formaldehyde hydrate, HOCH₂OH, and RNCH₂NH₂ (I) (R = H or organic radical) is validated by expts. in which HCHO and I are interchangeably used in reactions which are characteristic of the former. In each reaction studied, both reagents lead to the formation of the same chief product, the byproduct of the reactions with I being the liberated amine corresponding to the H₂O formed when HCHO is used. The following I are used: methylenbis-p-toluidine (II), -p-chloroaniline (III), -p-bromoaniline (IV), -p-anisidine (V), -ethylaniline (VI), -piperidine (VII), and -morpholine (VIII); the last 3, having no amino H, are NH₃ analogs of formaldehyde acetals. In some expts. the trimeric methylene-p-toluidine (IX) is used, giving the same products as obtained from II. The reaction may in some cases be reversible but no investigation is carried out in this regard. II, m. 93.5-5°. III, m. 64-6°. IV, m. 90-2°, and V, m. 63-5° are prepared according to Bischoff and Reinfeld (Ber. 36, 41(1903)); VI, m. 74-5°, according to v. Braun (C. A. 2, 2804); VII, b2 69-72°, in 90% yield, and VIII, b2 99-107°, in 69% yield, according to Ehrenberg (J. prakt. Chem. 36, 117(1877)). The following anthranililides are prepared by interaction of the corresponding amines and isatoic anhydride: N-phenyl- (X), m. 128.5-9°, N-p-bromophenyl- (XI), m. 154-5°, and N-p-anisylantranililide (XII), m. 123-3.7°. Reaction of 0.01 mol. N-(6-amino-α-methylp-toluidine and 0.01 mol. I, II, III, IV, V, VI, VII or VIII by refluxing in 50-90 cc. absolute EtOH for 1 h. gives 3-p-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (XIII), m. 139-41°, and the corresponding amines in the following yields: with II, 97% XIII and 86% p-MeC₆H₄NH₂ (Bz derivative m. 152-3°); with III, 76% and 86% p-ClC₆H₄NH₂ (Bz derivative m. 188°); with IV, 77% and 84% p-BrC₆H₄NH₂ (Bz derivative m. 201°); with V, 70% and 99% p-MeOC₆H₄NH₂ (Bz derivative m. 154.5-5°); with VI, 95% with VII 95% and 99% piperidine (HCl salt m. 242.5-4°); with VIII, 88% and 73% morpholine (HCl salt m. 168-72°); and with VII in the presence of EtONa, 25%. An experiment carried out with VII in the complete absence of moisture gives 92% XIII and 100% piperidine. XIII prepared with HCHO m. 139-41°. X (0.01 mol.) dissolved in 10-20 cc. EtOH containing NaOH and 2-5 cc. 37% HCHO, when warmed to 60° and chilled, gives 96% 3-phenyl-1,2-dihydro-4(3)-quinazoline (XIV), m. 176° or 180° (corrected). XI under the same conditions gives 82% 3-p-bromophenyl derivative (XV), m. 194-5° or 199-200° (corrected), and XII gives 91% 3-p-methoxyphenyl derivative (XVI), m. 185-5.5°. When X is treated with HCHO in alkaline EtOH at room temperature, 1-(hydroxymethyl)-3-phenyl-1,2-dihydro-4(3)-quinazoline (XVII), m. 109-10° or 110-11° (corrected, decomposition) is formed. It solidifies and remelts 172-5° after formation of XIV. When a solution of XVII in absolute EtOH is distilled, HCHO is liberated, identified as methylenedimethone, m. 190-1°, and XIV is formed. Interaction of o-NH₂CH₂CO₂H with HCHO in alkaline EtOH gives a compound (XVIII) m. 141°, in the absence of alkali, a product m. 65-70° with evolution of HCHO, resolidifying and subliming around 130°. XVIII when heated with H₂O or NH₄OH gives HCHO. Acidification of the solution of XVIII in NH₄OH with AcOH and treatment of the filtrate with Thatcher's reagent gives urotropine tetraiodide, m. 210° after darkening at 110-15° and shrinking at 165-70°. Mild oxidation of XVIII with KMnO₄ in Me₂CO gives 4(3)-quinazoline, m. 210-14° (picrate m. 206-8°), indicating that XVIII is 1,3-bis(hydroxymethyl)-1,2-dihydro-4(3)-quinazoline. The formation of XIV, XV and XVI by ring closure of X, XI and XII with I-VIII is studied under various conditions given, together with the results, in a table. The structure of XIV, XV

L7 ANSWER 46 OF 47 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The course of the condensation of CH₂O with PhNH₂ and p-MeC₆H₄NH₂ depends entirely on the ionic concentration of the medium in which the condensation takes place. Thus, methylenediacetylaminates, CH₂(NHAr)₂, (I) are formed at the concns. [H⁺] < 1 + 10⁻⁷, while tertiary bases, ArN:CH₂ (II), at [H⁺] ≥ 1 + 10⁻⁷. This change in the character of condensation products appears quite sharply and is already marked within the limits of H-ion concentration of 1-2 pH. In both cases the one base becomes contaminated with the other; thus, II formed at pH 7 contains some I, and I formed at pH 7 contains II. These admixts. of the two bases are very small and become smaller for the condensation with the greater deviation of H-ion concentration from the value pH 7. In the condensation in the medium [H⁺] > 1 + 10⁻⁷ near the value pH 7 the admixt. of I generally disappears. This fact is explained by the instability of I in media with an acid concentration of H ions. I is changed to II under H₂O and on boiling with alc. with the separation of ArNH₂ (Ann. 302, 335). These transformations proceed more rapidly with the higher H-ion concentration and the higher temperature. Contrary to Eibner (Ber. 30, 1448), the proportions of the reacting CH₂O and arylamines do not affect the course of condensation. I is as easily obtained with a double excess of CH₂O in a medium [H⁺] < 1 + 10⁻⁷ as with the theoretical amount of CH₂O. It follows that the scheme of the formation of II by Eibner is incorrect, and I is not formed as an intermediate product in the preparation of II, because the reaction CH₂(NHAr)₂ + CH₂O → 2ArN:CH₂ + H₂O is impossible in the medium [H⁺] < 1 + 10⁻⁷, while the formation of I with an excess of an amine is impossible with good distilled H₂O with [H⁺] near 1 + 10⁻⁷, for under these conditions II is formed. CH₂(NHCH₂Me-p)₂ is obtained in 80-90% yield by interaction of 0.05 mole of CH₂O (30%) and 0.1 mole of p-MeC₆H₄NH₂ in 100 cc. of H₂O or a buffer solution with [H⁺] = 1 + 10⁻⁸; the filter cake, dried and recrystd. from dilute alc., m. 89°. Condensation at [H⁺] = 1 + 10⁻⁹ gives a pure product after 1 crystallization. Identical results are obtained by using an excess of CH₂O, CH₂(NC₆H₄Me-p) is obtained in 80% yield as above from 1 mole of CH₂O and 1 mole of p-MeC₆H₄NH₂ in H₂O or buffer solution with [H⁺] = 1 + 10⁻⁷. CH₂(NHPh)₂, m. 64-5°, is obtained from 0.1 mole of PhNH₂ and 0.05 mole of CH₂O in H₂O or buffer solution with [H⁺] < 1 + 10⁻⁷. CH₂NHPh, prepared from 0.1 mole of PhNH₂ and 1 mole of CH₂O in 200 cc. of H₂O with [H⁺] ≥ 1 + 10⁻⁷, m. 107° and 200°. Conversion of CH₂(NHCH₂Me-p)₂ to CH₂(NC₆H₄Me-p)-CH₂(NHCH₂Me-p)₂ (1.5 g.), m. 89-90°, pulverized and allowed to stand 4 hrs. at room temperature in 40 cc. of H₂O with [H⁺] = 1 < 10⁻⁴, then filtered, washed with H₂O and recrystd. from alc., gives a mixture, m. 129-30° and 200°. The conversion can be accelerated with an increase of temperature and the concentration of H ions.

ACCESSION NUMBER: 1932:51374 CAPLUS
 DOCUMENT NUMBER: 26:51374
 ORIGINAL REFERENCE NO.: 26:5293c-1
 TITLE: Condensation of formaldehyde with aromatic amines
 AUTHOR(S): Drozdov, N. S.
 SOURCE: Zhurnal Obshchei Khimii (1931), 1, 1171-6
 CODEN: ZOIKHA; ISSN: 0044-460X
 DOCUMENT TYPE: Journal

L7 ANSWER 47 OF 47 CAPLUS COPYRIGHT 2005 ACS on STN
 GI For diagram(s), see printed CA issue.
 AB cf. C. A., 8, 127. In attempting to methylate the 2 compds. (I) and (II) with HCHO (Leuckhardt, Ber., 22, 1851, and earlier papers; Eschweiler, Ber., 38, 880), not only was a Me group introduced but the CHOH group was oxidized quant. to C=O; the reaction is general, AcMe being formed when iso-PrOH is heated with HCHO and NEH₂ or piperidine. Thus, 5.6 g. (I) in 10 cc. H₂O acidified with conc. HCl, when heated 4 hrs. at 115-20° with 5 cc. of 40% HCHO, gave 5.4 g. 1- α -N-methylpyrrolidylpropane-1-one (III). b14 69-74°, b21 80-2°, very hygroscopic, has an unpleasant, strongly basic and narcotic odor, slowly turns yellowish in the light in corked vessels; its superheated vapors color a fir splinter moistened with HCl red; it is stable towards KMnO₄ in H₂SO₄, at once decomposed by alks., at once gives a Ag mirror with a drop of concentrate AgNO₃ and at once ppt. Au from neutral AuCl₃ solution while from its aqueous HCl solution AuCl₃ ppts. the chloroaurate in yellow microscopic needles, m. 106° (corrected). The base is volatile with steam and can be distilled under atmospheric pressure. Oxime, b14 140°, picrate of the oxime, reddish brown syrup. Picrate of (I), long yellow needles, sinters about 95°, m. 103° (corrected). In the prepare of (II), a much more effective Pt sponge is obtained when, after the decantation with distilled H₂O to disappearance of the Cl reaction, it is washed with the solvent to be used in the reduction. If it is filtered off, at once transferred to the vacuum desiccator and dried and air then admitted to the desiccator, it always warms up and cakes, its efficiency being thus decreased. With 0.5 g. of the sponge prepared in the new way, 3.60 g. of pyrrole base absorbed 1166 cc. H (15-7°, 756 mm.) in 16 hrs.; calculate, 1254.2 cc. (0°, 760 mm.). With Pd, the reduction is not confined to the pyrrole nucleus but extends to the side chain, giving a mixture of (II) and 1- α -pyrrolidylpropane, b765 145-50°, has a piperidine-like, strong narcotic odor. From 2.5 g. of (II) in 5 cc. acidified H₂O heated 4 hrs. at 115-20° with 6 cc. of 40% HCHO is obtained 2 g. of 1- α -N-methylpyrrolidylpropane-2-one (synthetic dl-hygrine), b14 79-83°, b21-2 89-92°, can be kept for weeks in corked tubes without change; its Superheated vapor gives a red color with a fir splinter moistened with HCl while its aqueous HCl solns. are without action; it has a piperidine-like odor, is stable towards KMnO₄ in dilute H₂SO₄, at once decomposed by alks., at once gives Ag₂O with AgNO₃ and a mirror on warming, can be distilled under atmospheric pressure. Picrate, yellow needles, begins to sinter 162°, m. 174° (corrected). Liebermanns (Ber., 22, 677) gives 148° as the m. p. of the picrate of natural hygrine. A purer sample of the hygrine (L., Ber., 28, 579) was found by H. to b11-2 79-81°, [α]_D20 1.2°, but still gave too high values for N (10.54%; calculate, 9.93) and gave a picrate m. 158° (corrected). Oxime of (IV). m. 125° (corrected); L. (Ber., 26, 852) gives 116-20° for the oxime of natural hygrine. H₂NCHMe₂CH₂Ac, b0.14 25° without decompose, is reduced in 1-2 hrs. by alc. and 3-4 times the calculate amount of Na to H₂NCHMe₂CH₂CHMeOH, b16 70-5°. 5.7 g. of which, heated 4 hrs. at 115-20° in 10 cc. acidified H₂O with 13 cc. of 40% HCHO, gives 4 5-5.0 g. of diacetone-methylamine, MeNHCHMe₂CH₂Ac. b15 50-3°, has a menthol-like odor and produces dizziness and headache when inhaled deeply.
 ACCESSION NUMBER: 1914:6107 CAPLUS
 DOCUMENT NUMBER: 8:6107
 ORIGINAL REFERENCE NO.: 8:934e-1,935a-e
 TITLE: Synthesis of hygrine. If. Synthesis of the racemic hygrine. A new oxidation method. Further communications on the catalytic reduction of pyrrole

=> d his

(FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005

L1 1 S FORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005

L2 61794 S 50-00-0/RN

L3 166261 S N-METHYL?

L4 1415128 S ?AMINE

L5 889 S L2 AND L3 AND L4

L6 362618 S DISTILL?

L7 47 S L5 AND L6

=> s formaldehyde

135103 FORMALDEHYDE

371 FORMALDEHYDES

L8 135208 FORMALDEHYDE

(FORMALDEHYDE OR FORMALDEHYDES)

=> s l8 and l2

L9 53548 L8 AND L2

=> s l8 or l2

L10 143454 L8 OR L2

=> s l10 and l3

L11 3718 L10 AND L3

=> s l11 and l4

L12 2315 L11 AND L4

=> s l12 not l7

L13 2268 L12 NOT L7

=> s l13 and l6

L14 36 L13 AND L6

=> d l14 1-36 abs ibib

L14 ANSWER 1 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB The polyamines, useful as intermediates for the manufacture of isocyanates,
 are

manufactured by (a) reacting PhNH₂ with HCHO at resp. mol. ratio 1:(1.5-20)
 in

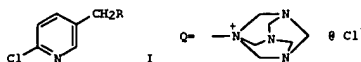
acidic ionic liquid, (b) removing the ionic liquid from the reaction
 mixture and
 (c) recycling the ionic liquid to the reaction stage. Thus, adding HCHO
 (32% solution) dropwise to PhNH₂ (PhNH₂/HCHO mol. ratio 3.0) at 80°,
 removing the H₂O by azeotropic distillation at 80° in vacuo and
 heating the reaction mixture at 80-120°/100 mbar gave a
 precondensate. This was diluted with PhNH₂, added dropwise over 30 min at
 35° to a mixture of ionic liquid (preparation from AlCl₃ and
 1-butyl-3-methylimidazolium chloride given) and o-xylene and the whole was
 stirred for 60 min at 35°, 60 min at 60° and 10 h at
 120° to give reaction products comprising 2 liquid phases. The lower
 phase containing the ionic liquid was separated and returned to the
 precondensate

rearrangement reaction step and the upper phase was worked up to give
 title polyamines in 35-45% yields.

ACCESSION NUMBER: 2002:941574 CAPLUS
 DOCUMENT NUMBER: 138:25096
 TITLE: Manufacture of polyamines of diphenylmethane series in
 presence of ionic liquids
 INVENTOR(S): Koch, Daniel; Schellhaas, Michael; Grotjohann, Dirk
 PATENT ASSIGNEE(S): Bayer AG, Germany
 SOURCE: Ger. Offen., 6 pp.
 CODEN: GWXXEX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 10127273	A1	20021212	DE 2001-1012723	20010605
PRIORITY APPLN. INFO.: DE 2001-1012723 20010605				

L14 ANSWER 2 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
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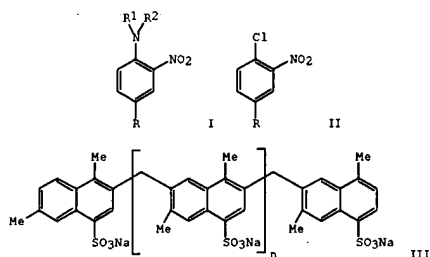
AB The title compds. (I; R = N:CH₂), useful as an intermediate for drugs and
 agrochems., in particular insecticides, are prepared by (1) reaction of
 2-chloro-5-trichloromethylpyridine, hexamethylenetetramine, and
 H in the presence of a hydrogenation catalyst or (2) hydrolysis of
 2-chloro-5-pyridylmethylhexamethylenetetrammonium chloride I (R = Q) with
 H₂O. I (R = N:CH₂) is hydrolyzed to 2-chloro-5-aminomethylpyridine I (R =
 NH₂) in the presence of a lower alc. while the byproduct
 formaldehyde is converted into di(lower alkoxy)methane and removed
 outside the reaction system. Thus, 2-chloro-5-trichloromethylpyridine
 46.2, hexamethylenetetramine 56.0, Et₃N 60.6, Raney nickel 4.6,
 H₂O 84.5, and PhMe 46.2 g were added to an autoclave and stirred at
 45° for 5 h while introducing H at 3 + 105 Pa to give 65.4% I
 (R = N:CH₂) and 12.0% I (R = Q) vs. 4.2% I (R = N:CH₂) and 79% I (R = Q)
 when the reaction was carried out in the absence of Et₃N. The byproduct I
 (R = Q) 9.1, 28% aqueous NH₃ 1.83, H₂O 11.5, and PhMe 6.9 g were added to a
 reactor and heated at 60° for 2 h to give 99.4% I (R = N:CH₂) and
 0.6% unreacted I (R = Q). I (R = N:CH₂) (7.7 g) was suspended in 11.5 g
 PhMe, and to the suspension was added dropwise 15.6 g 36% concentrated
 aqueous HCl

at 30° over 10 min and then added 12.8 g MeOH and the reaction
 mixture was stirred at 66° for 1 h and further reacted while
 distilling off MeOH and dimethoxymethane under normal pressure until
 the reaction temperature reached 100° and then neutralized with aqueous NaOH
 and extracted CHCl₃ to give 96% I (R = NH₂).

ACCESSION NUMBER: 1997:53901 CAPLUS
 DOCUMENT NUMBER: 126:74753
 TITLE: Method for producing N-methylidene
 -2-chloro-5-pyridinemethanamine
 INVENTOR(S): Aketada, Hiroyuki; Hitomi, Susumu; Matsunaga, Tomoko;
 Nagaoka, Masayo
 PATENT ASSIGNEE(S): Kosei Chemical Co, Japan
 SOURCE: Jpn. Kokai Tokyo Koho, 7 pp.
 CODEN: JKKXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 08295670	A2	19961112	JP 1995-181738	19950718
PRIORITY APPLN. INFO.: JP 1995-39825 A 19950228				
OTHER SOURCE(S): CASREACT 126:74753				

L14 ANSWER 3 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
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AB Nitroanilines I (R = H, NO₂; R₁, R₂ = H, Cl-4 alkyl) are prepared by
 aminolysis/ammonolysis of nitrochlorobenzenes II with 2000-4000 mol%
 HNHR₂ at 40-120° under atmospheric or elevated pressure in the presence
 of 0.1-10 weight% (vs. II) of an ionic or nonionic surfactant. For example,
 1.83 mol 2-O₂NCH₂Cl was added over 4 h to 4.02 mol HNMe₂ (as 40% solution)
 and 10 g dimethylnaphthalenesulfonate-formaldehyde condensate
 III (n undefined) at 55-60°, followed by stirring 8 h at
 60-70°, workup, and vacuum distillation, to give 93.2%
 2-O₂NCH₂NMe₂ of 98.8% purity. Three addnl. examples are described, with
 94.5-99.1% yields.

ACCESSION NUMBER: 1991:428869 CAPLUS
 DOCUMENT NUMBER: 115:28869
 TITLE: Preparation of nitroanilines by ammonolysis or
 aminolysis of nitrochlorobenzenes in the presence of
 surfactants
 INVENTOR(S): Papenfuhr, Theodor; Hess, Reiner; Deubel, Reinhold;
 Jung, Ruediger
 PATENT ASSIGNEE(S): Hoechst A.-G., Germany
 SOURCE: Ger., 6 pp.
 CODEN: GWXXAW
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 3924092	C1	19901129	DE 1989-3924092	19890720
CA 2063817	AA	19910121	CA 1990-2063817	19900719
WO 9101292	A1	19910207	WO 1990-EP1180	19900719
W: CA, JP, US				
RW: AT, BE, CH, DE, DK, ES, FR, GB, IT, LU, NL, SE				
EP 483241	A1	19920506	EP 1990-911416	19900719

L14 ANSWER 3 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 04506805	T2	19921126	JP 1990-510846	19900719
PRIORITY APPLN. INFO.: DE 1989-3924092 A 19890720				
OTHER SOURCE(S): MARPAT 115:28869				
WO 1990-EP1180 W 19900719				

L14 ANSWER 4 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The title compns., with low evolution of HCHO, contain 8-methylol derivs. of amides, urethanes, ureas, or aminotriazines, or their ethers, and BF₃, BF₃ complexes, HBF₄, or its salts. Stirring 70% aqueous 4,5-dihydroxy-N,N'-bis(hydroxymethyl)ethylene urea 2000, MeOH 580, and 51% methanolic BF₃.MeOH 25 g at pH 1.6 and 40° for 4 h, cooling, adding 38.2 g 25% NaOH, and distilling MeOH at 40°/60-80 mm gave a 75% aqueous finish with pH 5.7. Cotton poplin (basis weight 140 g/m²) was treated (uptake 70%) with this solution containing 10 g/L MgCl₂.6H₂O and dried at 110° to 8% residual H₂O to give a fabric with dry wrinkle recovery (DIN 53 890) 233, tenacity 270 N, and residual HCHO (AATCC 112) 154 ppm; vs. 254, 276, and 695, resp., when MeOH was omitted, and 110, 406, and 7, resp., to unfinished poplin.

ACCESSION NUMBER: 1991:410792 CAPLUS
 DOCUMENT NUMBER: 115:10792
 TITLE: Process for the production of aqueous solutions suitable for finishing cellulose-containing textile materials
 INVENTOR(S): Bereck, Attila; Flory, Klaus; Kummer, Matthias
 PATENT ASSIGNEE(S): BASF A.-G., Germany
 SOURCE: Eur. Pat. Appl., 9 pp.
 CODEN: EPXXUW
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 392349	A1	19901017	EP 1990-106514	19900405
EP 392349	B1	19940112		
R: AT, BE, CH, DE, DK, ES, FR, GB, IT, LI, NL, SE				
DE 3912084	A1	19901025	DE 1989-3912084	19890413
CA 2013060	AA	19901013	CA 1990-2013060	19900326
AT 100122	E	19940115	AT 1990-106514	19900405
ES 2047740	T3	19940301	ES 1990-106514	19900405
US 6001132	A	19991214	US 1990-504881	19900405
JP 02292249	A2	19901203	JP 1990-92362	19900409
JP 3130811	B2	20010131		
PRIORITY APPL. INFO.:			DE 1989-3912084	A 19890413
			EP 1990-106514	A 19900405
OTHER SOURCE(S):			MARPAT 115:10792	

L14 ANSWER 6 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The title polyamines are prepared with decreased energy consumption in distillation by polymerization of PhNH₂ with HCHO followed by a series of extraction stages. A schematic diagram of the process is given. The 2-stage polymerization of PhNH₂ with HCHO in the presence of HCl followed by continuous countercurrent extraction with a PhNH₂-xylene mixture, a 2nd extraction, washing, and distillation, gave a mixture of 4,4'-methylenedianiline 46.3, 2,2'- and 2,4'-isomers 4.5, N-Me derivs. 0.2, trisamines 22.2, tetraamines 11.1, and polyamines with higher d.p. 15.6%.

ACCESSION NUMBER: 1989:633936 CAPLUS
 DOCUMENT NUMBER: 111:233936
 TITLE: Preparation of polynuclear aromatic polyamines
 INVENTOR(S): Knoefel, Hartmut; Brockelt, Michael; Petinaux, Marcel; Uchdorf, Rudolf
 PATENT ASSIGNEE(S): Bayer A.-G., Fed. Rep. Ger.
 SOURCE: Eur. Pat. Appl., 14 pp.
 CODEN: EPXXUW
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 337205	A2	19891018	EP 1989-105652	19890330
EP 337205	A3	19901212		
EP 337205	B1	19930113		
R: BE, DE, ES, FR, GB, IT, NL				
DE 3812083	A1	19891026	DE 1988-3812083	19880412
CA 1318076	A1	19930518	CA 1989-595201	19890330
ES 2053848	T3	19940801	ES 1989-105652	19890330
US 4924028	A	19900508	US 1989-335062	19890406
BR 8901716	A	19891121	BR 1989-1716	19890411
JP 02124855	A2	19900514	JP 1989-89891	19890411
PRIORITY APPL. INFO.:			DE 1988-3812083	A 19880412

L14 ANSWER 5 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Simple tests were evaluated for use in determining the condition and lifetime of industrial solvents such as cold dipping solvents (Stoddard solvent), vapor degreasing solvents (chlorinated hydrocarbons), and metal preparation or precision cleaning solvents (Freon 113 and isopropanol). The use of these tests to monitor the quality of reclaimed solvents was also explored. Visible absorption spectrometry was the most reliably measured property, followed by sp. gr., viscosity, and elec. conductivity To determine the concns. of antioxidants, acid acceptors, and metal stabilizers in chlorinated solvents, gas chromatog.-mass spectrometry was used. Reclamation studies on spent chlorinated solvents were carried out by using distillation and a carbon adsorption method.

ACCESSION NUMBER: 1990:534614 CAPLUS
 DOCUMENT NUMBER: 113:134614
 TITLE: Methods for monitoring solvent condition and maximizing its utilization
 AUTHOR(S): Joshi, Surendra B.; Donahue, Bernard A.; Tarrer, Arthur R.; Guin, James A.; Rahman, Mahmud A.; Brady, Bill L., Jr.
 CORPORATE SOURCE: U S Air Force (HQ AFESC/RDVS), Tyndall Air Force Base, Panama City, FL 32403-6001, USA
 SOURCE: ASTM Special Technical Publication (1989), 1043(Hazard. Ind. Solid Waste Minimization Pract.), 80-103
 CODEN: ASTTAS; ISSN: 0066-0558
 DOCUMENT TYPE: Journal
 LANGUAGE: English

L14 ANSWER 7 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB N-glycidylamines with high purity, low viscosity and improved storing properties are prepared by 2-stage addition of amines to epichlorohydrin (I) first at 65° to 60% conversion of functional groups and second at 66-120° followed by dehydrochlorination of the chlorohydrins with an alkali hydroxide. Thus, a mixture of 279.3 g aniline, 624 g 97.8% I, 300 g iso-BuCOMe, and 27 g water was heated to 60°, kept for 3 h, then at 85° for 5 h, cooled to 50°, treated with 750 g 40% NaOH for 4 h and finally heated 2 h at 80°. Treating the reaction mixture with 650 g water, then with 300 g iso-BuCOMe, washing the mixture 3 times with 225 g 5% salt, and distilling off iso-BuCOMe gave 590 g N,N-diglycidylaniline with 8.69 epoxy group equivalent/kg, 0.48% Cl, and viscosity 110 mPa-s/25°.

ACCESSION NUMBER: 1989:555027 CAPLUS
 DOCUMENT NUMBER: 111:155027
 TITLE: Preparation of aromatic N-glycidylamines
 INVENTOR(S): Dobas, Ivan; Lunak, Stanislav; Makovsky, Leopold; Podzimek, Stepan; Macku, Vladislav; Rada, Antonin; Machovsky, Stanislav
 PATENT ASSIGNEE(S): Czech., 12 pp.
 SOURCE: Czech. CODEN: CZXXGA9
 DOCUMENT TYPE: Patent
 LANGUAGE: Czech
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 256646	B1	19880415	CS 1986-3580	19860516
PRIORITY APPL. INFO.:			CS 1986-3580	19860516
OTHER SOURCE(S):			MARPAT 111:155027	

L14 ANSWER 8 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Ge adsorbent resins were prepared by polymerization of triethylenetetramine with epichlorohydrin followed by *N*-methylation with HCHO. The adsorption of Ge⁴⁺ onto the resins at different pH and in the presence of other metal ions (Ni²⁺, Zn²⁺, Fe²⁺) was studied. The resins were regenerated by washing with HCl followed by distilled water.
 ACCESSION NUMBER: 1989:174267 CAPLUS
 DOCUMENT NUMBER: 110:174267
 TITLE: Synthesis and adsorption of germanium adsorption resin
 AUTHOR(S): Fei, Wen; Liang, Liang
 CORPORATE SOURCE: Hunan Univ., Changsha, Peop. Rep. China
 SOURCE: Lizi Jiaohuan Yu Xifu (1988), 4(3), 190-3
 CODEN: LUYKRE; ISSN: 1001-5493
 DOCUMENT TYPE: Journal
 LANGUAGE: Chinese

L14 ANSWER 9 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB The title compds. H2C:CR1CONHCH2OR2 (R1 = H, Me; R2 = Bu, CH2CHMe2, CHMeEt, CHMe3), useful as crosslinking monomers for coatings, are manufactured by hydroxymethylating H2C:CR1CONH2 with HCHO in R2OH in the presence of an alkaline catalyst, etherifying the resulting H2C:CR1CONHCH2OH with addnl. R2OH in the presence of an acid catalyst, and distilling off the solvent at pH 2-5. Thus, 71.7 g acrylamide was treated with 56.3 g paraformaldehyde in 37.1 g BuOH at pH 10.0 (by Et3N) at 50° to give *N*-methylolacrylamide (I), which was treated with addnl. 425.2 g BuOH under reflux at pH 3.0 (by oxalic acid). The reaction mixture was readjusted at pH 3.0 by oxalic acid and concentrated under reduced pressure at 90° to give 163.2 g product containing *N*-butoxymethylacrylamide 98.2, I 0.3, and acrylamide 1.5%.
 ACCESSION NUMBER: 1988:205254 CAPLUS
 DOCUMENT NUMBER: 108:205254
 TITLE: Method of making *N*-alkoxymethyl(meth)acrylamides
 INVENTOR(S): Watanabe, Seiichi; Sakasai, Kazuya; Tanaka, Yoshinori
 PATENT ASSIGNEE(S): Mitsui Toatsu Chemicals, Inc., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 5
 CODEN: JKKXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63005068	A2	19880111	JP 1986-146828	19860625
JP 07033362	B4	19950412		

PRIORITY APPLN. INFO.: JP 1986-146828 19860625
 OTHER SOURCE(S): CASREACT 108:205254; MARPAT 108:205254

L14 ANSWER 10 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB An ester (mono/di) of sucrose and p-[(HOCH2)2NCO]C6H4CO2H (I), sucrose etherified with (HOCH2)2NCOCH2CH2 and HOCH2NHCOCH2CH2 groups, a diester of sucrose and H2NCO(CH2)4CO2H, or a similar carbohydrate derivative is polymerized with HCHO and urea or melamine to prepare crosslinked resins with good elasticity and processability. Thus, 90 parts urea in 125 parts 37% HCHO solution was heated to 60°, adjusted to pH 8-9 with Na2CO3, heated for 45 min, mixed with an ester (mono/di) of sucrose and 1 10, NH4Cl 1, and cellulose fibers or powder 30 parts, freed of solvent by distillation, dried at <50° in vacuo, and heated at 80° to prepare a molding composition which gave moldings with elastic modulus 49,583 daN/cm2.
 ACCESSION NUMBER: 1981:16573 CAPLUS
 DOCUMENT NUMBER: 94:16573
 TITLE: Crosslinked resins from *N*-methylol group-containing carbohydrate derivatives
 INVENTOR(S): Greber, Gerhard; Andres, Hans; Pichler, Werner
 PATENT ASSIGNEE(S): Evidenzbuero Oesterreichischer Zuckerfabriken G.m.b.H., Austria
 SOURCE: Austrian, 8 pp.
 CODEN: AUXKAX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
AT 359287	B	19801027	AT 1979-2747	19790412
AT 7902747	A	19800315		
DE 2928003	A1	19801023	DE 1979-2928003	19790711
			AT 1979-2747	A 19790412

PRIORITY APPLN. INFO.:

L14 ANSWER 11 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Carpets from polyacrylonitrile (I) [25014-41-9] and polypropylene [9003-07-0] fibers were made flameproof by treatment with a mixture of a phosphate, e.g. tris(2,3-dibromopropyl) phosphate (II) [126-72-7] and the reaction product of a methylolmelamine derivative, e.g. hexamethylolmelamine pentamethyl ether (III) [13822-63-4] and a phosphonopropionamide, e.g. *N*-methylol-3-(dimethylphosphono)propionamide (IV) [20120-33-6]. Thus, 211 parts IV and 71 parts 90% III were heated 50 min at 118-25.deg. (the last 30 min in vacuo), MeOH distilled, and 220 parts II added at 100.deg. to give a clear, viscous product. A 1 carpet (1500 g/m2) was padded with a 45% solution of the above product (100% impregnation), dried at 90.deg., heated 5 min at 155.deg., washed (for improvement of hand) in a bath containing 5 g Na2CO3/l. and 2 g 1:5 mole p-tert-C9H19CGH4OH-ethylene oxide adduct 20 min at 40.deg., and dried at 90.deg. to give a flameproof (DIN 51 960) carpet.
 ACCESSION NUMBER: 1972:60868 CAPLUS
 DOCUMENT NUMBER: 76:60868
 TITLE: Flameproofing of carpets
 INVENTOR(S): Mayer, Fritz; Nachbur, Hermann; Kern, Joerg; Maeder, Arthur
 PATENT ASSIGNEE(S): Ciba-Geigy A.-G.
 SOURCE: Ger. Offen., 40 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2109702	A	19710930	DE 1971-2109702	19710302
CH 703541	A4	19720131	CH 1970-354170	19700310
CH 523373	A	19720531	CH 1970-523373	19700310
IL 36308	A1	19740516	IL 1971-36308	19710301
ZA 7101385	A	19720223	ZA 1971-1385	19710303
NO 129008	B	19740211	NO 1971-810	19710303
FR 2081816	A5	19711210	FR 1971-7974	19710308
FR 2081816	B1	19740215		
PL 83046	P	19751231	PL 1971-146733	19710308
BE 763974	A1	19710909	BE 1971-100659	19710309
NL 7103132	A	19710914	NL 1971-3132	19710309
AT 319181	B	19741210	AT 1971-2023	19710309
GB 1331346	A	19730926	GB 1971-23110	19710419
			CH 1970-3541	A 19700310

PRIORITY APPLN. INFO.:

L14 ANSWER 12 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB 1,3-Propanolamine was mixed at 40° with aqueous HCHO, and the solution was continuously fed into a tubular reactor, containing a catalyst with 17.5% Co, 0.9% Cr and 0.36% P2O5 on SiO2, at 300 atm H pressure and 140°. The mixture was distilled to give 90 weight % N,N-dimethyl-1,3-aminopropanol. Similarly prepared were PhCH2NMe, N-methylmorpholine, tetramethylethylenediamine, N,N-dimethyl-1,3-propylenediamine, N-methylcyclohexylamine and N-methylpiperidine.

ACCESSION NUMBER: 1971:124791 CAPLUS
 DOCUMENT NUMBER: 74:124791
 TITLE: Secondary and tertiary amines
 PATENT ASSIGNEE(S): Badische Anilin- & Soda-Fabrik AG
 SOURCE: Fr. Demande, 8 pp.
 CODEN: FRXXBL
 DOCUMENT TYPE: Patent
 LANGUAGE: French
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 2017634		19700522	FR	
DE 1793380			DE	
GB 1276740			GB	
PRIORITY APPLN. INFO.:			DE	19680909

L14 ANSWER 13 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Hard, elastic coatings and films are prepared by mixed polycondensation of polyesters of mol. weight 600-3000 with aminoplast resins. Thus, a polyester (I) of acid number 12.2 mg KOH/g is prepared by polycondensation of 1,4-bis(hydroxymethyl)cyclohexane (II) and ethylene glycol with phthalic anhydride (III) and adipic acid (IV) and modification with maleic anhydride (V). Melamine, paraformaldehyde, BuOH, and HCO2H are refluxed to obtain a clear solution, which is treated with a 60% xylene solution of I and the reaction mixture distilled to yield a coating composition, which is pigmented with TiO2 and sprayed onto metals to yield a hard elastic coating. Other polyesters used are prepared by condensing II and 1,2-propanediol with III and IV and modifying with V or III. Other aminoplast resins used are prepared by condensing urea with HCHO and BuOH or iso-PROH.

ACCESSION NUMBER: 1971:14269 CAPLUS
 DOCUMENT NUMBER: 74:14269
 TITLE: Coating compositions containing a hydroxyl and carboxyl polyester and a N-methylol polymer
 INVENTOR(S): Schuetze, Ernst C.; Riemhofer, Franz; Dittmann, Walter
 PATENT ASSIGNEE(S): Chemische Werke Huels A.-G.
 SOURCE: Ger. Offen., 16 pp. Addn. to Ger. Offen. 1644769
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 2
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1900414	A	19700924	DE 1969-1900414	19690104
DE 1900414	B2	19770505		
DE 1900414	C3	19771229		
JP 49020611	B4	19740525	JP 1969-54204	19690710
PRIORITY APPLN. INFO.:			DE 1968-1811632	A 19681129
			DE 1969-1900414	A 19690104

L14 ANSWER 14 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Polyepoxides are cured with a reaction product of a dihydroxydiphenyl sulfone, an amine, and an aldehyde. Thus, 1000 g. 37% aqueous solution of HCHO was added during 60 min. to 2222 g. of an aqueous solution of Me2NH at <30°. After addition of HCHO, the mixture was stirred 2 hrs. at 25-30°. To 1044 g. of this mixture, was added 250 g. 4,4'-dihydroxydiphenyl sulfone. This mixture was slowly heated to reflux under atmospheric pressure and refluxed for 2 hrs. The contents were then distilled at 50 mm. to a pot temperature of 120°. The residue, 447 g., was wine-colored, and cooled to a brittle solid at approx. 25°. Similarly prepared were curing agents from N-methylethanamine and bis(3-aminopropyl) ether of diethylene glycol and from 3,3'-dimethyl-4,4'-dihydroxydiphenyl sulfone. The curing agents produced by this method are used in the conventional manner.

ACCESSION NUMBER: 1967:19200 CAPLUS
 DOCUMENT NUMBER: 66:19200
 TITLE: Polyepoxide curing agents
 INVENTOR(S): Sellers, Ralph F.
 PATENT ASSIGNEE(S): Union Carbide Corp.
 SOURCE: U.S., 8 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3285991		19661115	US	19630326

L14 ANSWER 15 OF 36 CAPLUS COPYRIGHT 2005 ACS on STN
 AB The title compds. I and the intermediates II and salts thereof are prepared by standard methods and are useful as tranquilizers, psychic stimulants, diuretics, antihistamines, and inhibitors of pseudocholinesterase and O-methyltransferase. Salts with H2SiF6 are useful as moth-killing agents and derivs. with thiocyanate-formaldehyde condensation products as pickling inhibitors. Thus, to a mixture of 600 g. 1-bromo-2-nitrobenzene, 300 g. anthranilic acid, and 300 ml. n-amyl alc. was added with stirring at 80-90° 3.0 g. Cu powder and 300 g. K2CO3. The temperature rose to 120° and the mixture was heated 3 hrs. at 200-10° and worked up to yield 92% N-(2-nitrophenyl)anthranilic acid (III), m. 219° (AcOH). A mixture of 348 g. III in 10 l. dry MeOH was treated with stirring 7 hrs. on a steam bath with gaseous HCl to yield 86% methyl N-(2-nitrophenyl)anthranilate (IV), m. 156-7° (MeOH). A solution of 299.2 g. IV in 8 l. absolute MeOH was hydrogenated 24 hrs. with 100 ml. Raney Ni suspension and 3.5 atmospheric H at 25° to yield 85% methyl N-(2-aminophenyl)anthranilate (V), m. 102-3° (EtOH-H2O). V (169.4 g.) was heated 1 hr. in an oil bath at 240-50° and worked up to yield 86% 5H-dibenzo[b,e][1,4]diazepin-11(10H)-one (VI), m. 254-5° (CSH5N). To a solution of 139.0 g. 3-bromopropanol in 200 ml. absolute MeOH was added dropwise in 10 min. with stirring under N a solution of 121.2 g. N-benzyl-methylamine in 50 ml. absolute MeOH. After 20 min., the solution started refluxing for 1 hr. and was then heated 16 hrs. with stirring under reflux, to yield 151.7 g. (from 2 reactions) 3-(N-benzylmethylamino)propanol (VII), b.p. 15-0.17 94-7° n25D 1.5203. To a solution of 150 g. VII in 200 ml. dry C6H6 was added dropwise with stirring under N in 1 hr. a solution of 200 g. SOCl2 in 100 ml. dry C6H6. The mixture was refluxed 8 hrs. to yield after 3 days at 25° 120.6 g. 3-(N-benzylmethylamino)propylchloride (VIII), b.p. 60 104.5-6° n25D 1.5150; VIII.HCl m. 86-93°. Similarly were prepared 3-dibenzylaminopropanol, 3-dibenzylaminopropyl chloride and its HCl salt. To a solution of 31.5 g. VI in 450 ml. dioxane (distilled from LiAlH4) was added with stirring 6.0 g. NaNH2 in small portions in 1 hr., and the mixture was refluxed 3.5 hrs. To this mixture was added dropwise at 70° in 30 min. 20.4 g. freshly distilled 2-diethylaminoethyl chloride and the mixture was refluxed 4 hrs. to yield 67% 10-(2-diethylaminoethyl)-5H-dibenzo[b,e][1,4]diazepin-11(10H)-one (IX), m. 132-3° (iso-PROH). Similarly were prepared the following 10-substituted 5H-dibenzo[b,e][1,4]diazepin-11(10H)-ones (substituent, yield, and m.p. given): 3-dimethylaminopropyl (X), 50%, 119-21°; 3-N-benzylmethylaminopropyl (XI), --- (from VI, VII, and NaNH in DMF); 3-diethylaminopropyl (XII), ---, 77-8°. A solution of 40.0 g. XI in 400 ml. absolute MeOH was hydrogenolyzed 16 hrs. at 3.8 atmospheric over 4.0 g. 10% Pd-C to yield 10-(3-methyl-aminopropyl)-5H-dibenzo[b,e][1,4]diazepin-11(10H)-one (XIII).-HCl, hygroscopic solid. To a mixture of 6.1 g. IX in 250 ml. dry Et2O was added with stirring under N 1.1 g. LiAlH4; the mixture was refluxed 30 hrs. to yield 71% 10-(2-diethylaminoethyl)-10,11-dihydro-5H-dibenzo[b,e][1,4]diazepine-2HCl, m. 199.5-200.5° (decomposition). Similarly were prepared the following 10-substituted 10,11-dihydro-5H-dibenzo[b,e][1,4]diazepines (starting compound, substituent, yield salt, and m.p. given): X, 3-dimethylaminopropyl, ---, di-HCl, 176-7°; XIII, 3-methylaminopropyl, ---, di-HCl, hygroscopic solid (iso-PROH-Et2O); VI, H, 60%, ---, 196.5-201° (iso-PROH); XII, 3-diethylaminopropyl, ---, di-HCl, ---. Starting with the appropriate substituted aminoalkyl chlorides were prepared the following 10-substituted 5H-dibenzo[b,e][1,4]diazepin-11(10H)-ones (substituent given, and the

L14 ANSWER 15 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
GI corresponding 10-substituted 10,11-dihydro-5H-dibenzo[b,e][1,4] diazepines
AB (and HCl salts, no phys. consts. given): 3-dibenzylaminopropyl (XIV) (no
dihydro deriv. prepd.); 2-(diethylamino)ethyl; 2-diisopropylaminoethyl;
2-dimethylaminoethyl; 4-dimethylaminobutyl; 2-(1-pyrrolidyl)ethyl;
2-(2,2-dimethyl-1-pyrrolidyl)ethyl; 3-(4-methyl-1-piperazinyl)propyl;
2-(1-piperidyl)ethyl; 2-(4-propyl-1-piperidyl)ethyl; 2-
hexamethylenimino)ethyl; 2-(2-methylhexamethylenimino)ethyl;
2-(4-morpholinyl)ethyl; 2-(2-methyl-4-morpholinyl)ethyl;
2-(4-thiamorpholinyl)ethyl; 3-aminopropyl (from XIV, using the method for
XIII). Also were prepd. the following substituted III (substituent given,
no phys. consts.): 5-Cl; 4-Cl; 3-Me; 4-tert-Bu; 6-F; 4,5-Me2; 3-MeO-4-Me;
4-EO. The following N-(2-nitro-substituted phenyl)anthranilic acids were
also prepd. (substituent given): 4-tert-Bu; 3-EO; 4,5-F2; 4,5(BuO)2;
4,5,6-(MeO)3; 5-CF3. Prepd. were N-(4-chloro-2-nitrophenyl)-5-
chloroanthranilic acid and N-(4-methoxy-2-nitrophenyl)-5-
methoxyanthranilic acid; the corresponding Me, Et, Pr, and Bu esters of
these anthranilic acids; the corresponding amino esters. Also prepd. were
the following substituted VI: 4-Me; 3-Cl; 3-tert-Bu; 7,8-F2; 8-tert-Bu;
6,7,8-(MeO)3; 7-CF3; 9-Et; 2-Cl; 1-F; 2,3-Me2; 4-MeO-3-Me; 3-EO; 2,8-Cl2;
2,8-(MeO)2; 7,8-(BuO)2. Also prepd. were the corresponding 10,11-dihydro
substituted 5H-dibenzo[b,e][1,4]diazepines. The substituted VI were
converted with 3-dimethylaminopropyl chloride into the corresponding
10-(3-dimethylaminopropyl)-substituted 5H-dibenzo[b,e][1,4]diazepin-
11(10H)-ones, and reduced to yield the corresponding 10,11-dihydro-10-(3-
dimethylaminopropyl)-substituted 5H-dibenzo[b,e][1,4]diazepines and di-HCl
salts. Cf. CA 63, 2859h and 14641g.

ACCESSION NUMBER: 1966:43917 CAPLUS
DOCUMENT NUMBER: 64:43917
ORIGINAL REFERENCE NO.: 64:8218g-h,8219a-h
TITLE: Substituted 10,11-dihydro-5H-dibenzo [b,e] [1,4]
diazepines
PATENT ASSIGNEE(S): Upjohn Co.
SOURCE: 40 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 297030		19650525	NL	
PRIORITY APPLN. INFO.:			US	19620828

L14 ANSWER 17 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
GI For diagram(s), see printed CA Issue.
AB 3-Aminoalkyl-substituted indazoles (I) which, by analogy with
tryptamine and hydroxytryptamine, might be expected to
have similar biol. activity, were prepared. The simple analogs (R = H or OH,
R1 = CH2CH2NH2) were prepared by Ainsworth (CA 52, 3785b, 11011f) from the
corresponding indazole-3-carboxylic acid derivs. The present authors
sought to prepare such compds. by applying a Mannich reaction with
formaldehyde and ammonia or an amine to 3-methylindazole
I (R = H, R1 = Me), but without success. Nor could they induce
3-benzylindazole, which they prepared in two ways from o-bromophenyl benzyl
ketone and N-nitroso-o-acetamidobenzyl, resp., to undergo this reaction.
They sought therefore to obtain from o-nitroacetophenone the Mannich
bases, β -dimethylaminoethyl (IIa), β -piperidylethyl (IIb), and
 β -(3-methylcyclohexylamino)ethyl (IIc)
o-nitrophenyl ketone with a view to converting them to
3-(β -dimethylaminoethyl), 3-(β -piperidylethyl), or 3-(β -
3-methylcyclohexylamino)ethylindazoles by the Fischer
method, viz., reduction of the NO2 group, diazotization, reduction to the
hydrazine, and ring closure. The Mannich bases obtained in salt form,
however, differed from those obtained in this way by Mannich and Dannehl
(CA 32, 62336) and were identified, by empirical formula, spectrographic
measurements, and reaction with ozone, as compds. formed by reaction of a
second mol. of HCHO and having the structure III. Despite varying the
conditions, they were not able to obtain IIIa. Their own base IIIa
resinified immediately on liberation from its salt. On subjecting its HCl
salt to the above mentioned series of reactions (Fischer) without
isolation of intermediates and at acid pH throughout, there were obtained
the expected 3-(N-substituted- β -aminoisopropyl)indazoles
corresponding to formula I, in which R is H and R1 is CHMeCH2NRR1,
remembering that the methylene is reduced to Me. If the Mannich reaction
is applied to the homologous o-nitropropiofenone, then the
N-substituted- β -aminomethyl group should add on to the CH2 proximal
to the CO and form a Mannich base corresponding to III, with the methylene
reduced to Me. This on undergoing the same Fischer reactions as before
should produce the same 3-(N-substituted- β -aminoisopropyl)indazoles.
Although the authors obtained one of these by using Me2NH.HCl in the
Mannich reaction, it proceeded with such difficulty and the overall yield
was so small that its value as a structural proof was largely vitiated.
These 3- β -aminopropylindazole products, unlike the usual Mannich
bases, are stable. The benzoyl derivative of the dimethylamino product was
prepared and it was also nitrated to the 5-nitro derivative, but the
corresponding 5-amino derivative formed by hydrogenation proved to be
unstable. A comparable nitration and reduction of 3-methylindazole as a

model
substance produced however the known 5-aminomethylindazole. The following
are the more important exptl. data. o-Bromophenyl benzyl ketone (50.7 g.)
heated 18 hrs. in a sealed tube with 80 ml. hydrazine hydrate at
200°, the product extracted into ether, washed with HOAc, KHCO3, and
water, and evaporated and the residue distilled at 155°/0.01 mm.
gave 14.5 g. 3-benzylindazole, prisms, m. 113-15° (ether/petr.
ether). Also, 16.5 g. o-nitroacetophenone refluxed with 6 g. HCHO and 8.2
g. Me2NH.HCl in 40 ml. HOAc 3 hrs., and the distilled in vacuo gave
21.4 g. IIIa.HCl, m. 213-15° (decomposition). This (1.08g.) in 3 ml.
HOAc, 10 ml. alc., and 2 ml. 2N HCl was hydrogenated in the presence of
0.2 g. 5% Pd-C at 26°/715 mm., and the residue crystallized from
iso-PrOH-ether to give a product, m. 118-24°. This di-HCl salt
(16.3 g.) in 50 ml. concentrated HCl diazotized with 4.2 g. NaNO2 in 40 ml.
water, then added during 30 min. portionwise to 500 ml. saturated aqueous

L14 ANSWER 16 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
GI For diagram(s), see printed CA Issue.
AB Amines with the general formula I, where n is 0-3, R1, R2, and R3 are H or
Me, R4 is an alkyl group, and R5 is H or an alkyl group, can be prepared
from an aminophenol with the general formula II, where R4' is H or an
alkyl group, and R5' is H, acyl, or an alkyl group, and alcohols of the
general formulas CH2:CHC(CH3)(OH)[CH2CH2CH2CH(CH3)]CH3 or
HOCH2CHC(CH3)(CH3)CH2CH2CH2CH(CH3)CH3 or their esters. Thus, to a mixture of
11. freshly distilled formic acid (99%) and 120 g.
2,3,5-trimethyl-4-formylaminophenol, 200 g. isophytol was added. With
addition of N2 and refluxing, mixture was stirred for 22 hrs. at 135°.
After cooling mixture was poured on 2 kg. ice and a brown oil formed. Yield
was 130 g. α -tocopheramine, b0.01 200-3°,
absorption maximum at 300 m μ (E11 85), which was acylated and then
reduced to give N-ethyl- γ -tocopheramine, a light yellow
oil, b0.01 211-14°, uv absorption maximum at 299 m μ (E11 52),
n24.5D 1.5096. Similarly obtained, starting with 2,3-dimethyl-4-
formylaminophenol, was N-ethyl- γ -tocopheramine, b0.05
195-7°, uv absorption maximum at 238 and 305 m μ (E11 195 and
69), n22.5D 1.5083. In 9 g. dry formic acid, 10 g. α -
tocopheramine and 6 g. of a 40% formaldehyde solution were
heated for 16 hrs. to boiling. Yield was N,N-dimethyl- γ -
tocopheramine, b0.02 200-5°, n23D 1.5015. Similarly
obtained, starting with δ -tocopheramine, was
N,N-dimethyl- δ -tocopheramine, b0.007 183-8°, n19D
1.5080, absorption maximum at 244 and 304 m μ (E11 268 and 58). In 1 l.
dry formic acid 174 g. N-formyl-2,3-dimethyl-4-aminophenol was dissolved
under N2, 220 g. isophytol was added, and the mixture refluxed for 22 hrs.
after which it was poured on 2 kg. ice. Yield was N-formyl- γ -
tocopheramine, b0.01 233°, n24.5D 1.5158, which was reduced
to yield N-methyl- γ -tocopheramine, a
light yellow oil, b. 190-5°, n22D 1.5083, absorption maximum at 306
m μ (E11 74). Similarly obtained, starting with N-formyl- δ -
tocopheramine, was N-methyl- δ -
tocopheramine, b0.005 189-90°, n22.5D 1.5106, uv absorption
maximum at 242 and 309 m μ (E11 225 and 66). Also obtained starting
with N-formyl- β -tocopheramine, was N-
methyl- β -tocopheramine, b0.03 207-10°, n21D
1.5088, absorption maximum at 234 and 300 m μ (E11 182 and 77). The
compds. are useful as anti-oxidants.

ACCESSION NUMBER: 1966:4088 CAPLUS
DOCUMENT NUMBER: 64:4088
ORIGINAL REFERENCE NO.: 64:707e-h,708a
TITLE: Amines
PATENT ASSIGNEE(S): F. Hoffmann-La Roche & Co., A.-G.
SOURCE: 9 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 6414649		19650621	NL	
PRIORITY APPLN. INFO.:			CH	19631220

L14 ANSWER 17 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
GI while SO2 was passed in and, after standing, concd. in vacuo to 200 ml.,
boiled, and then evapd. to dryness in vacuo, treated with NH4OH, extd.
into ether and then into dil. HOAc, and made alk. with NH4OH, and the
pptd. bases shaken with ether gave 8.8 g. I (R = H, R1 = CHMeCH2NMe2),
b0.01 122-3, recrystd. from petr. ether to give 5.5 g. prisms, m.
70-2°.

ACCESSION NUMBER: 1964:16678 CAPLUS
DOCUMENT NUMBER: 60:16678
ORIGINAL REFERENCE NO.: 60:2923e-h,2924a-d
TITLE: 3-(β -Aminopropyl)indazole derivatives
AUTHOR(S): Hunziker, F.; Lehner, H.; Schindler, O.; Schmutz, J.
SOURCE: Pharmaceutica Acta Helveticae (1963), 38(7-8), 539-46
CODEN: PAHEAA; ISSN: 0031-6865
DOCUMENT TYPE: Journal
LANGUAGE: German

L14 ANSWER 19 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Amino addition compds., effective in controlling hypertension, were prepared by heating a secondary or tertiary amine with a chloroacetylene to give amino acetylenes, which were catalytically hydrogenated to aminoethylenes and aminoethanes. Hydration of the aminoacetylenes gave amino ketones, from which the hydroxyamines were prepared by reduction. Thus, 46 g. Na in small chunks was added with stirring to about 3 l. liquid NH₃ while acetylene gas was passed into the liquid; after the bluish color had disappeared, 228 g. diisopropyl ketone was added, addition of C₂H₂ continued for about 4 hrs., 1 l. Et₂O added, the mixture kept overnight, 1 l. H₂O added, the Et₂O layer separated, dried, and distilled in vacuo in the cold, and the residue distilled to give 3-isopropyl-4-methyl-1-pentyn-3-ol, b₂₈ 80-83°, n_D 1.442. Also prepared were 3-methyl-1-heptyn-3-ol, b₁₄ 62-3°, n_D 1.434, 3,4,4-trimethyl-1-pentyn-3-ol, b₁₀₀ 88-90°, n_D 1.438, and 3,4-dimethyl-1-hexyn-3-ol, b₄₈ 75°, n_D 1.435. Chloroacetylenes were prepared according to the method of Hennion and Maloney (CA 47, 4781): 3-chloro-3-methyl-1-butyne, b. 74-6°, n_D 1.416; 3-chloro-3-isopropyl-4-methyl-1-pentyne, b₅₅ 92-7°, n_D 1.453; 3-chloro-3,4-dimethyl-1-hexyne, b₃₂ 67-77°, n_D 1.450; 3-chloro-3,4-dimethyl-1-pentyne, b₅₂ 54-55°, n_D 1.448; 3-chloro-3-methyl-1-heptyne, b₂₈ 64-68°, n_D 1.440; 3-chloro-3-methyl-1-hexyne, b₄₅ 54-55°, n_D 1.435; 3-chloro-3-ethyl-1-hexyne, b₃₇ 69-71°, n_D 1.443; 3-chloro-3,4-dimethyl-1-hexyne, b₆₆ 73-79°, n_D 1.454; 3-chloro-3,4,4-trimethyl-1-pentyne, b₉₄ 82°. Acetylenic amines were prepared by the method of Hennion and Nelson (CA 51, 12905h), to give the following substituted 3-methyl-1-butyne (substituents given): 3-isopropylamino, b. 115-18°, n_D 1.419, m. about 27° (HCl salt m. 204-6°, sulfate salt); 3-ethylamino, b. 108-9°, m. about 50.5° (HCl salt m. 183-5°, maleate salt); 3-propylamino, b. 129° (HCl salt m. 171-3°); 3-butylamino, b. 151°, m. 24°, n_D 1.428 (HCl salt m. 183-4°); 3-isobutylamino, b. 140-2°, m. about 19°, n_D 1.423 (HCl salt m. 215-16°); 3-sec-butylamino, b₆₇ 72°, n_D 1.425 (HCl salt m. 181-3°); 3-tert-butylamino, b₈₄ 72-2.5°, m. 24°, n_D 1.430 (HCl salt m. 221-3°); N,N-dipropyl-3-amino, b₁₉ 74°, n_D 1.436 (HCl salt m. 208-9°); 3-sec-amyl-amino, b. 66°, n_D 1.428 (HCl salt m. 133-5°); 3-tert-amylamino, b₆ 51°, n_D 1.437 (HCl salt m. 167-9°); 3-allylamino, b. 130° (HCl salt m. 194-5°); N-methyl-3-amino, b₁₃₅ 96-98°, n_D 1.435 (HCl salt m. 184-6°); N-methyl-N-tert-butyl-3-amino, b₁₃₀ 115-16°, n_D 1.450 (HCl salt m. 140-2°); N-ethyl-N-isopropyl-3-amino (HCl salt m. 177-9°). The following 3-substituted amino-3-methyl-1-pentyne (substituents given) were prepared: isopropyl, b₉₃ 77-7.5°, n_D 1.426 (HCl salt m. 196-7°); tert-butyl, b₂₅ 62°, n_D 1.435 (HCl salt m. 204-5°); isopropyl-4-methyl, b₅₀ 58-60° (HCl salt m. 179-81°); isopropyl-4,4-dimethyl, b₁₀₄ 110-30°, n_D 1.445 (HCl salt m. 198-9°); tert-butyl-4,4-dimethyl, b₂₈ 110-11°, n_D 1.457 (HCl salt m. 238°); tert-butyl-4-methyl, b₅₈ 96-8°, n_D 1.400 (HCl salt m. above 280°); ethyl-isopropyl (HCl salt m. 177-9°); methylisopropyl-4-methyl, b₂₀ 73-5°, n_D 1.445 (HCl salt m. 198-200°). The following 3-ethyl-1-pentyne (substituents given) were prepared: 3-isopropylamino, b₂₅ 71°, n_D 1.433 (HCl salt m. 222-3°); 3-tert-butylamino, b₂₃ 75°, n_D 1.440 (HCl salt m. 267-8°); 3-ethylamino, b₇₀ 77-9°, n_D 1.437 (HCl salt m. 205-7°); N-methyl

L14 ANSWER 19 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)

(HCl salt m. 126-7°); tert-butylamino (HCl salt m. 141-2°). 3-substituted 3-methyl-2-butanones (substituents given): tert-butylamino (HCl salt m. 154-6°); pyrrolidino, b₁₇ 99°, n_D 1.465; isopropylamino (HCl salt m. 125-7°). Also prepd. was 3-tert-butylamino-3-methyl-2-pentanol; HCl salt m. 126-7°. ACCESSION NUMBER: 1963:72932. CAPLUS DOCUMENT NUMBER: 58:72932 ORIGINAL REFERENCE NO.: 58:12420c-h, 12421a-f TITLE: Controlling hypertension INVENTOR(S): Easton, Nelson R.; Kornfeld, Edmund C. PATENT ASSIGNEE(S): Eli Lilly and Co. SOURCE: 17 pp. DOCUMENT TYPE: Patent LANGUAGE: Unavailable PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3067101		19621204	US	19591125
GB 921943			GB	

L14 ANSWER 19 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)

-N-isopropyl-3-amino (HCl salt m. 143-5°). The following 3-methyl-1-hexynes (substituents given) were prepd.: 3-isopropylamino, b₃₈ 73.5-5.5°, n_D 1.432 (HCl salt m. 167-9°); 3-tert-butylamino, b₈ 50-3°, n_D 1.439 (HCl salt m. 175-6°); 3-ethylamino-5-methyl (HCl salt m. 204°); 3-tert-butylamino-4-methyl, b₆ 53°, n_D 1.447 (HCl salt m. 174-5°). The following 4-methyl-1-pentyne (substituents given) were prepd.: 3-isopropylamino-3-isopropyl, b₅₂ 110-18°, n_D 1.450 (HCl salt m. 206-7°); 3-ethylamino-3-isopropyl, b₁₅ 68-81°, b₁₁ 76-81°. Also prepd. were: 4-tert-butyl-amino-4-methyl-2-pentyne, b₅₉ 90-2°, n_D 1.440 (HCl salt m. 145-6°); 3-tert-butylamino-3-ethyl-1-hexyne, b₈ 68°, n_D 1.447 (HCl salt m. 163-4°); 3-tert-butylamino-3-methyl-1-heptyne, b₁₀ 76°, n_D 1.441 (HCl salt m. 144-6°). The following ethylenic amines were prepd.: substituted 3-methyl-1-butenes (substituents given): 3-isopropylamino, b. 121-2, n_D 1.417 (HCl salt m. 115-16°); 3-tert-butylamino (HCl salt m. 202-4°); N-methyl-N-isopropyl-3-amino, b₁₀₇ 76-80°, n_D 1.434; 3-ethylamino, b. 110°, n_D 1.416 (HCl salt m. 138-40°). 3-Ethyl-1-pentenes (substituents given): 3-tert-butylamino (HCl salt m. 183-4°); 3-ethylamino, b₇₀ 84°, n_D 1.436 (HCl salt m. 167-9°); 3-isopropylamino, b₅₀ 89°, n_D 1.436 (HCl salt m. 196-8°). 3-Methyl-1-pentenes (substituents given): 3-tert-butylamino, b₂₅ 67°, n_D 1.437 (HCl salt m. 164-6°); 3-isopropylamino-4-methyl (HCl salt m. 101-5°); 3-ethylamino, b₁₁₀ 77°, n_D 1.427 (HCl salt m. 114-17°); 3-isopropylamino, b₉₀ 84°, n_D 1.428 (HCl salt m. 116-17°). The following satd. amines were reported: 3-substituted 3-methylbutanes (substituents given): ethylamino, b. 112-15°, n_D 1.405 (HCl salt m. 160-1°); tert-butylamino, b₆₁ 74°, n_D 1.418 (HCl salt m. 218-19°); 3-sec-butylamino (HCl salt m. 137-9°); 3-sec-amylamino (HCl salt m. 142-4°); 3-tert-amylamino (HCl salt m. 183-5°); methylisopropylamino, b₁₁₀ 90° (HCl salt m. 142-4°); isopropylamino, b₁₃₀ 78-80°, n_D 1.408 (HCl salt m. 131-2°). 3-Substituted 3-ethylpentanes (substituents given): tert-butylamino (HCl salt m. 172-3°); isopropylamino (HCl salt m. 217-18°); ethylamino, b₇₀ 88°, n_D 1.427 (HCl salt m. 189-91°). 3-Substituted 3-methylpentanes (substituents given): isopropylamino-4-methyl (HCl salt m. 183-4°); isopropylamino-4,4-dimethyl (HCl salt m. 183-4°); ethylamino, b₁₁₀ 81°, n_D 1.419 (HCl salt m. 164-6°); isopropyl-amino, b₉₀ 87°, n_D 1.421 (HCl salt m. 194-6°); tert-butylamino, b₂₅ 70°, n_D 1.429 (HCl salt m. 195-6°). Also prepd. were: 3-ethylamino-3-isopropyl-4-methylpentane (HCl salt m. 195-6°); 3-isopropylamino-3-methylhexane (HCl salt m. 113-15°); 3-tert-butylamino-3-methylhexane (HCl salt m. 142-4°); and 2-tert-butylamino-2-methylpentane, b₅₈ 90-1°, n_D 1.423 (HCl salt m. 136-8°). The amino ketones, prepd. by hydration of the corresponding acetylenes with aq. H₂SO₄ and mercuric oxide as catalysts, were given as follows: 3-substituted 3-methyl-2-pentanones (substituents given): tert-butylamino (HCl salt m. 152-4°); isopropylamino (HCl salt m. 99-101°). 3-Substituted 3-ethyl-2-pentanones (substituents given): isopropylamino (HCl salt m. 135-6°); tert-butylamino (HCl salt m. 173-5°). 3-Substituted 3-methyl-2-butanones (substituents given): tert-butyl-amino, b₅₈ 104°, n_D 1.434 (HCl salt m. 208°); isopropylamino (HCl salt m. 131-3°). The amino alcs. were prepd. by NaBH₄ redn. of the secondary or tertiary amino ketones in alc., or with LiBH₄ in Et₂O. 3-substituted 3-ethyl-2-pentanol (substituents given): isopropylamino

L14 ANSWER 20 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN

AB Amidomethylated aromatic amines (Ar(CH₂NHCO₂R)), are prepared For example, 15.9 g. 85% H₃PO₄ heated at 65-70° until the endothermic reaction subsides then at 85-90° 4 hrs, cooled, poured into stirred cold H₂O, filtered, washed, and dried yields 76% crude 4,6-bis(acrylamidomethyl)-m-xylene. Replacing I by N-methylolacetamide yields 4,6-bis(acetamidomethyl)-m-xylene (II), m. 252-6°. From 22.5 ml. H₂SO₄, 105 ml. HOAc, and 71.5 g N, N'-methylenebisacetamide, m. 197-8° prepared from acetamide and formaldehyde in xylene at about 130°, heated 5.5 hrs. at 90° gives N-(2,4-dimethylbenzyl)acetamide, m. 113-12.5° (C₆H₆). Diacetamidomethyl ether (III), m. 97-98.5° (dioxane), is prepared from 418 g. acetamide (IV), 360 g. paraformaldehyde (V), and 1000 ml. xylene refluxed with vigorous stirring in a flask with a trap for H₂O formed, until 121 ml. H₂O is collected. Heating 65 g. III with 17 ml. H₂SO₄ and 78 ml. HOAc 5.5 hrs., cooling, and diluting with dilute NH₄OH gives II. From 118 g. IV, 66 g. V, and 3 ml. 40% aqueous KOH heated 15 min. at 60° poured into 500 ml. HOAc plus 500 ml.

Ac₂O, heated 15 hrs. at 100° and distilled in vacuo is formed, after removal of excess reagents, N-(acetoxymethyl)acetamide (VI), b₈ 117-25°, n_D 1.4451. VI reacted with m-xylene, H₂SO₄, and HOAc 4 hrs. at 85-90° to give II. N-(Chloromethyl)acetamide, m-xylene, and anhydrous ZnCl₂ refluxed about 3 hrs. and poured into dilute NH₄OH gives N-(2,4-dimethylbenzyl)acetamide. A mixture of 496 g. II, 250 ml. H₂SO₄, and 2.1 H₂O is refluxed with agitation 33.5 hrs., cooled, extracted with C₆H₆, the precipitate filtered off, and the aqueous layer neutralized with NaOH solution. Continuous extraction with C₆H₆ 5 hrs., with BuOH 4 hrs., removal of solvents, and purification gives 4,6-bis(aminomethyl)-m-xylene (VII), m. 139-40°. VII. 2HCl, m. 305-10° in Tetralin treated with phosgene at 200-05° 5-7 hrs. gives after distillation, mainly 4,6-bis(isocyanato methyl)-m-xylene. The latter reacts with polyesters to form polyurethan resins.

ACCESSION NUMBER: 1962:455998 CAPLUS DOCUMENT NUMBER: 57:55998 ORIGINAL REFERENCE NO.: 57:11099g-1, 11100a-b TITLE: Amidomethylation of aromatic compounds INVENTOR(S): Parris, Chester L. PATENT ASSIGNEE(S): Pittsburgh Plate Glass Co. SOURCE: 5 pp. DOCUMENT TYPE: Patent LANGUAGE: Unavailable PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3024282		19620306	US	19571029
GB 891771			GB	

L14 ANSWER 21 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB N,N-disubstituted 2-aminobutane-1,4-diols were prepared and subjected to ring closure to form 3-(N,N-disubstituted-amino)tetrahydrofurans, intermediates for quaternary ammonium compds. with neurophysiol. properties. Propargyl tetrahydropyranyl ether (81.5 g.) in absolute Et2O was treated at 0° with stirring with 37 g. BuLi or 49 g. PhLi in Et2O, the mixture stirred 2 hrs. at 0°, then stirred until room temperature was attained, the mixture added dropwise under N to a stirred solution of 100 g. (EtCO)2CO in absolute Et2O at -85° and left 14 hrs. to give γ-propionylpropargyl tetrahydropyranyl ether (I), b0.04 64-6°. I (24.6 g.) dissolved in absolute Et2O, treated with 10 ml. dry NMe2, the mixture left for 14 hrs. at room temperature, excess NMe2 and Et2O removed in vacuo, and the residue distilled in vacuo yielded γ-propionyl-β-dimethylaminoethyl tetrahydropyranyl ether (II), b0.02 110° (bath temperature), m. room temperature (AcOEt). II (29.2 g.) hydrogenated in AcOH in the presence of Pt, the mixture filtered, AcOH removed in vacuo, the residue extracted with Et2O and dissolved in water, the solution brought to pH 12 and extracted with Et2O, yielded a mixture of 8-hydroxy-β-dimethylamino-n-hexyl tetrahydropyranyl ether, 8-hydroxy-β-dimethylamino-n-hexanol, and their Ac derivs. The mixture (6.3 g.) was dissolved in 33 ml. sirupy H3PO4 (d. 1.7) and 100 ml. water, the solution heated 1 hr., brought to pH 14, and steam-distd., the distillate neutralized with N HCl, evaporated to dryness in vacuo, and the residue made alkaline and continuously extracted with Et2O, yielded 3-dimethylamino-5-ethyltetrahydrofuran, b10-11 602°. To 6.1 g. stirred and cooled 90% formic acid 3.8 g. dl-2,5-dimethyl-2,5-dihydroxy-3-aminohexane was added dropwise, followed by 4.22 g. 37% aqueous formaldehyde, the mixture heated to 95° for 12 hrs., cooled to 5°. 2 ml. concentrated HCl added dropwise, and the mixture evaporated to dryness in vacuo. The residue was dissolved in 40 ml. water, the solution treated with activated C, filtered, brought to pH >11 and continuously extracted with Et2O to yield dl-2,5-dimethyl-2,5-dihydroxy-3-dimethylaminohexane (III), b0.0025 60-5°. III (2 g.) treated at 0-10° with 4 ml. 33 volume-% H2SO4, the mixture heated 4 hrs. at 95°, diluted with 10 ml. water, brought to pH >11 and continuously extracted with Et2O yielded dl-2,2,5,5-tetramethyl-3-dimethylaminotetrahydrofuran, b11 56-7°.

ACCESSION NUMBER: 1961:131369 CAPLUS
 DOCUMENT NUMBER: 55:131369
 ORIGINAL REFERENCE NO.: 55:24791e-1
 TITLE: Tertiary amines derived from tetrahydrofuran
 INVENTOR(S): Eugster, Conrad H.; Denss, Rolf; Hafliiger, Franz; Hofer, Bruno; Pfister, Rudolf; Zimmermann, Markus
 PATENT ASSIGNEE(S): J. R. Geigy Akt.-Ges.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CH 349615		19601215	CH	

L14 ANSWER 22 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L14 ANSWER 22 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB cf. CA 46, 4490b; 53, 90861; 55, 19814b. In order to obtain detailed information concerning the structures of the intermediates in carbonium ion type interconversions of the title compds., the extent of isotope-position rearrangement in the reactions of cyclopropylcarbinylammonium-C14 (I) with HNO2 and cyclopropylcarbinol-x-C14 (II) with Lucas reagent was investigated. Cyclopropylmagnesium bromide was carbonated with C14O2 and the acid (III) converted to the amide, which was reduced to I. II was prepared by LiAlH4 reduction of III. The studies showed that the 3 CH2 groups in the starting material achieved a high degree of equivalence between reactants and products. This was best reasoned by assuming a rapid equilibrium of 3 isomeric nonclassical unsymmetrical bicyclobutonium ion intermediates. The degradation of allylcarbinyl-x-C14 chloride (IV) was done by treating 6.9 g. IV with 50 ml. 87% HCO2H (V) and 17.0 g. 30% H2O2. The mixture was stirred at 50° until clear (30 min.), then stirred 2 hrs., removed in vacuo, and methanolic HCl added to the residue. The mixture was refluxed 1 hr., HCO2Me and MeOH removed, and 6.1 g. 4-chloro-1,2-butanediol-x-C14 (VI), n25D 1.4760, distilled, b0.8 117°, n25D 1.4735. Hydrolysis of the intermediate formate with KOH gave 3-hydroxytetrahydrofuran, b7 61-2°, n25D 1.4396; phenyl carbamate m. 117.2-17.6°. VI (0.66 g.), 1.13 g. NaIO4, and 50 ml. H2O left 2 hrs. at room temperature, extracted with Et2O, and the aqueous layer added to 0.74 g. methone in 200 ml. H2O gave 0.38 g. formaldehyde-C14 dimethone, m. 191.6-2.6°. IV (4.66 g.) was converted into the Grignard reagent (1.44 g. Mg in 20 ml. Bu2O) and treated with 6.0 g. H2SO4 in 20 ml. H2O, the resulting 1-butene heated at 110° with 30 ml. 87% V and 11.3 g. 30% H2O2 and worked up to give 1,2-butanediol-x-C14 (VII), b12 90°, n25D 1.4396; bis(phenylcarbamate) m. 116-17°. A mixture of 0.516 g. VII and NaIO4 was treated as before, continuously extracted with Et2O, and the aqueous layer found to contain formaldehyde 84% dimethone. The Et2O extract was stirred with 0.98 g. NaOH, 0.12 g. NaOH, and 25 ml. H2O for 30 min., filtered, decolorized with NaHSO3, and the Et2O removed. The aqueous layer was treated with 30 g. Na2SO4, and steam distilled until 300 ml. distillate was collected. The distillate was neutralized with NaOH, evaporated, and 0.87 g. salt obtained. A portion was converted to the p-bromophenacyl propionate-x-C14, m. 61.4-2.8°, and the remainder treated with 0.6 ml. H2SO4 and 0.0028 mole NH3 in CHCl3 at 50° to analyze the gas for C14 (as BaCO3), and the acid-CHCl3 mixture treated with p-BrC6H4SO2Cl to give 76% N-ethyl- and 24% N-methyl-p-bromobenzenesulfonamide. Demination of I was accomplished by the method of R. and M. (CA 46, 1453a). The demination products were degraded by treating MnO4 and identifying the oxidation products. Degradation of cyclobutanol-x-C14 was also studied in order to assure the reliability of the methods of degradation.

ACCESSION NUMBER: 1961:18139 CAPLUS
 DOCUMENT NUMBER: 55:18139
 ORIGINAL REFERENCE NO.: 55:22160c-1,22161a
 TITLE: Small-ring compounds. XXIII. The nature of the intermediates in carbonium ion-type interconversion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives
 AUTHOR(S): Mazur, Robert H.; White, William N.; Semenov, Dorothy A.; Lee, C. C.; Silver, Mare S.; Roberts, John D.
 CORPORATE SOURCE: California Inst. of Technol., Pasadena
 SOURCE: Journal of the American Chemical Society (1959), 81, 4390-8

L14 ANSWER 23 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diamine(s), see printed CA issue.
 AB The peroxide obtained by Girssewald and Siegens (CA 15, 2416) from N2H4, HCHO, and H2O2, and claimed to be CH2.O.O.CH2.NN:CH2, actually had twice this mol. weight both in PhNO2 and in dioxane, and had the structure I. The O in I and other cyclic peroxides was determined iodometrically. ECNH2 (0.05 mol) and 0.1 mol HCHO (30% in H2O) cooled and treated with 2.5 cc. AcOH and then with 7 cc. 30% H2O2 gave 2 g. (C4H9NO2)n, viscous oil, whose cryoscopic mol. weight in C6H6 was approx. 610. N,N'-Dimethylolurea (1.2 g.) (m. 130°) in 25 cc. H2O, 10 cc. 30% H2O2, and 10 cc. concentrated HNO3 gave 0.34 g. (C3H6N2O3)n, m. 185-7° (decomposition), insol. in all organic solvents and identical with the compound made from urea by the method of G. and S. (loc. cit.). Difficulties in accepting a monomeric structure were discussed. (MeNH)2.2HCl (5 g.) cooled and treated 2 h. with 3.3 g. NaOH in 15 cc. H2O and 4 cc. 40% HCHO, saturated with K2CO3, and extracted with Et2O gave 1.56 g. 1,2,4,5-tetramethylhexahydro-sym-tetrazine (II), b11 58-60°, n20D 1.4695; picrate m. 115-16.5° (EtOH). Formed similarly was 10% tetraisopropyl homolog of II, m. 57-8° (petr. ether), camphorlike odor. (MeNH)2.2HCl (5 g.) and 3.63 g. Me2NNH2.2HCl was cooled and treated with 5 g. NaOH in 20 cc. H2O, followed by 8 cc. 40% HCHO, to give on Et2O extraction 1.35 g. II. A similar mixture of these amine salts with aqueous NaOH and HCHO (as above) was added dropwise to 100 g. solid NaOH and distilled to give 93% N-methylene-N',N'-dimethylhydrazine, b760 71-2°, n20D 1.4312 (Klages, et al., CA 35, 43459). o-C6H4.CH2.CH2.N.NMe.CH (isohydrazone) (5 g.) was refluxed in 25 cc. 2N H2SO4, the mixture cooled, and extracted with Et2O. The aqueous phase at 0° was treated successively with 5 cc. 40% HCHO, 5 cc. perhydrol, and 25 cc. 3.5N AcONa to give at 0° 4.7 g. III, m. 71-1.5° (decomposition) (petr. ether); picrate m. 91-3°, which with NH3 and ether was reconverted to III. The following reactions were carried out at 0°. (MeNH)2.2HCl (5.35 g.) in 40 cc. 3.4N AcONa was treated 5 min. with 8 cc. 40% HCHO and 4 cc. 30% H2O2, the mixture kept 5 min. without cooling then cooled to 0°, saturated with AcOK.ACOH (m. 148°) [Melsens, Ann. 52, 274(1844)], extracted 4 times with Et2O, these exts. combined and extracted with saturated Na2SO4, the dried Et2O solution at 0° shaken with active C, filtered, and evaporated in vacuo under anhydrous conditions to give CH2.NMe.NMe.CH2.O.O (IV), pale yellow oil, crystallizing when cooled with dry ice, m. -20° (pentane). IV treated with 1-methyl-6,8-dithio-1,2-dihydroquinoline in AcOH gave 70% bis(1-methyl-6,8-dinitro-1,2-dihydro-2-quinolyl) peroxide, decomposed at 120-24° (previously given as 128°). IV with tetrahydrophthalazine-HCl in an acetate-buffered solution gave di(o-xylylene)hexahydrodiazine (CA 54, 14263c). Formed similarly to IV were 64% N,N'-diethyltetrahydro-4,5-dioxapyridazine, m. 26°, n20D 1.4438, and 52% N,N'-diiso-Pr homolog, m. -1 to 2° (pentane). 26 refs.

ACCESSION NUMBER: 1961:8158 CAPLUS
 DOCUMENT NUMBER: 55:8158
 ORIGINAL REFERENCE NO.: 55:16441,1645a-g
 TITLE: Cyclic peroxides from hydrazine derivatives
 AUTHOR(S): Schmitz, Ernst
 CORPORATE SOURCE: Deut. Akad. Wiss., Berlin-Adlerhof
 SOURCE: Ann. (1960), 635, 73-82
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 175°, needles, m. 55° (petr. ether). XI (35 g.) and 400 cc. HBr (d. 1.5) boiled 24 hrs. so that 200 cc. of the acid distilled through a column, the cooled residue poured into H₂O, partially neutralized with NaOH, extd. with Et₂O, the ext. washed with H₂O and NaOH soln., and evapd. gave 6-bromo-1-phenyl-1-hexanone (XII), b.p. 124°, m. 33-35°. XII (15 g.) and 10 g. I warmed on the steam bath 1 hr., the cooled soln. dissolved in dil. HCl, the soln. washed with Et₂O, made alk. with NaOH, extd. with Et₂O, and the ext. evapd. gave 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-hexanone (XIII), b.p. 170°, oxalate m. 215°. XIII treated with 2-thienyllithium as in the prepn. of VII gave 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-hexanol (XIV), b.p. 08 215-20°, oxalate, prisms, decomp. at 178-80° (EtOH). XIV (5 g.) in 25 cc. CHCl₃ slowly satd. with HCl gas, kept 1 hr. at room temp., and the dried soln. evapd. at low temp. yielded 6-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-hexene-2HCl (XV), hygroscopic needles, decomp. at 210° (EtOH-EtOAc); oxalate, prisms, m. 175° (EtOH). Refluxing XV in MeOH soln. with MeI pptd. on addn. of EtOAc N1-[6-phenyl-6-(2-thienyl)hex-5-enyl]-N1, N1, N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, m. 161-3°. Et acrylate (50 g.), 71 g. I, and 50 cc. EtOH refluxed 8 hrs. gave Et β-[methyl(2-piperidinoethyl)amino]propionate (XVI), b.p. 161°. XVI treated with thienyllithium in the usual way gave 3-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-propanol (XVII), b.p. 184-8°; oxalate decomp. at 193°. XVII dehydrated as in the prepn. of XV gave 3-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-propene (XVIII); hydrochloride, prisms, m. 218° (EtOH); oxalate, prisms, m. 202° (80% EtOH). Refluxing with MeI in MeOH gave N1-[3,3-di(2-thienyl)prop-2-enyl]-N1, N1, N2-trimethylethylene-1-ammonium-2-piperidinium diiodide (XIX), needles, m. 183-4° (MeOH). The following compds. were prepd. similarly to the prepn. of XVII-XIX: 3-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-propanol, pale yellow oil, b.p. 05 180° (oxalate decomp. at 182°); 3-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-propene (XX) (oxalate m. 212-13°); N1-[3,3-di(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, m. 168° (EtOH); 3-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-propanol, light yellow oil, b.p. 05 165° (oxalate decomp. at 172°); 3-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-propene (XXI) [oxalate, prisms, m. 205° (90% EtOH)]; and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[3,3-di(2-thienyl)prop-2-enyl]ethylene-1,2-diammonium diiodide, needles, m. 172° (EtOH). Acrylonitrile (24 g.) added slowly to 56 g. 3-morpholinopropylamine and the mixt. kept overnight at room temp. gave 2-cyanoethyl(3-morpholinopropyl)amine (XXII), b.p. 180°. Formaldehyde (30 cc. 40%) added to 70 g. XXII in 35 cc. 90% HCO₂H, the mixt. heated 4 hrs. on the steam bath, NaOH soln. added, and the oil which sepd. pyrolyzed 3 hrs. at 270° gave methyl(3-morpholinopropyl)amine (XXIII), b.p. 120°, n_D 20 1.4715. XXIII treated as in the prepn. of XVII-XIX gave: 3-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-propanol, b.p. 05 200-2°, m. 77° (petr. ether) (oxalate m. 192-3°); 3-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-propene-2-HCl, decomp. at 233-4° (oxalate decomp. at 205-6°); and N1-[3,3-di(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-3-morpholinium diiodide, m. 184°. Et 6-bromohexanoate (20 g.) and 20 g. I warmed to 60° until reaction set in and the temp. rose spontaneously to 80°, the mixt. heated 2 hrs. on the steam bath after the reaction subsided, cooled, acidified, the acid soln. washed with Et₂O, basified at 0° with aq. NH₄, extd. with Et₂O, and the ext.

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 AB The preparation was described of diquaternary compds., which were ganglion-blocking agents. Acetophenone (12 g.), 4.5 g. paraformaldehyde, and 14.2 g. methyl(2-piperidinoethyl)-amine (I) in 30 cc. absolute EtOH acidified to Congo red with concentrated HCl, refluxed 1 hr., 3 g. paraformaldehyde added, the solution refluxed 2 hrs., and the cooled solution diluted with Me₂CO precipitated.
 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-propanone-2HCl (II), needles, m. 201-2° (MeOH); free base prepared by treatment with aqueous alkali and extraction with Et₂O. 2-Bromopyridine (15.8 g.) in 20 cc. Et₂O added with stirring in an atmosphere of dry N to a solution of BuLi from 1.75 g. Li and 10 g. BuCl at -60°, an anhydrous solution of the free base from 10 g. II added after 5 min., the temperature allowed to rise to -20° during the next 30 min., the product added to ice, the mixture acidified with HOAc, the aqueous phase washed with Et₂O, made alkaline with NaOH, extracted with Et₂O, and the extract evaporated yielded 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)-1-propanol (III), light brown oil, b.p. 05 190-5°, oxalate m. 201° (EtOH). III (5 g.) in 15 cc. 85% H₂SO₄ heated on the steam bath 15 min., the cooled solution diluted with H₂O, basified with aqueous NH₃, and extracted with petr. ether gave on evaporation of the extract 3.5 g.
 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)-1-propene (IV), dark brown oil. IV (3.5 g.) in 50 cc. HOAc shaken under H at 50°/1 atmospheric with 1 g. 3% Pd-C until 250 cc. H was absorbed, the filtered solution diluted with H₂O, made alkaline with aqueous NH₃, and extracted with Et₂O gave on evaporation of the extract 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-pyridyl)propane (V), b.p. 05 164-5°, oxalate m. 189°. MeI (1.6 g.) added to 2 g. V in 15 cc. MeOH precipitated after 16 hrs. N1,N1,N2-trimethyl-N1-[3-phenyl-3-(2-pyridyl)propyl]ethylene-1-ammonium-2-piperidinium diiodide (VI), cream-colored needles, m. 179° (MeOH). The dried Et₂O solution of the free base from 40 g. II added during 5 min. to a cooled stirred solution of 2-thienyllithium (from 33.6 g. thiophene, 0.4 mole BuLi, and 200 cc. Et₂O), stirring continued 30 min. in the cold, and the mixture poured on ice gave 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)-1-propanol (VII), pale yellow oil, b.p. 15 220°, oxalate decomp. at 190°. VII (10 g.) and 100 cc. 2N HCl kept 18 hrs. at room temperature, NaOH solution added, and the oil extracted with Et₂O gave 3-[methyl(2-piperidinoethyl)amino]-1-phenyl-1-(2-thienyl)propene (VIII), pale yellow oil, b.p. 1 176-80°; oxalate m. 208°. VIII treated as in the preparation of VI gave N1-[3-phenyl-3-(2-thienyl)prop-2-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, m. 195° (MeOH). KOH (52.5 g.) in 90 cc. H₂O added to 690 g. 1,5-dibromopentane, 141 g. phenol, and 500 cc. EtOH, the mixture refluxed 2 hrs., the solvent removed in vacuo, H₂O added to precipitate a heavy oily layer, the latter separated, washed with H₂O, dried, and distilled yielded 1-bromo-5-phenoxypentane (IX), b.p. 176-8°. NaCN (96 g.) in 100 cc. H₂O added to 400 g. IX in 400 cc. EtOH, the mixture refluxed 2 hrs., the solvent evaporated, and the product isolated with Et₂O gave 1-cyano-5-phenoxypentane (X), b.p. 196-8°. X (96 g.) in anhydrous Et₂O (200 cc.) added to a solution of PBr₃ (from 22.8 g. Li and 234 g. PBr₃ in 1000 cc. Et₂O), the solution refluxed 2 hrs., the cooled solution poured on ice, acidified, and steam distilled yielded 6-phenoxyl-1-phenyl-1-hexanone (XI), b.p. 2

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 evapd. gave Et 6-[methyl(2-piperidinoethyl)amino]hexanoate (XXIV), b.p. 05 130°. XXIV treated as in the prepn. of XVII-XIX yielded: 6-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXV), b.p. 05 205°; 6-[methyl(2-piperidinoethyl)amino]-1,1-di(2-thienyl)-1-hexene, b.p. 1 180° [oxalate decomp. at 186° (EtOH)]; and N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-piperidinium diiodide, leaflets, m. 163° (EtOH).
 6-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXVI), b.p. 05 205-10°, was prepd. by the method for prepn. of XXV. Oxalic acid (5 g.) in 20 cc. EtOH added to a hot soln. of 5 g. XXVI in 150 cc. EtOH and the slurry heated 5 min. on the steam bath pptd. the oxalate, decomp. at 200°, of 6-[methyl(2-pyrrolidinoethyl)amino]-1,1-di(2-thienyl)-1-hexene, converted as in the prepn. of XIX to N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, platelets, m. 97° (EtOH).
 6-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-hexanol (XXVII), pale yellow oil, b.p. 08 194-6°, was prepd. by the method for prepn. of XXV. XXVII was converted as in the prepn. of XVIII and XIX to 6-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-hexene (XXVIII), b.p. 05 169-71° (picrate, needles, m. 153° (EtOH)), and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[6,6-di(2-thienyl)hex-5-enyl]ethylene-1,2-diammonium diiodide, plates, m. 115° (EtOH). The following series of compds. was similarly prepd.: 6-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-hexanol, m. 66° (petr. ether); 6-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-hexene (hydrochloride m. 210-12°, oxalate decomp. at 191-3°); and N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-3-morpholinium diiodide, hygroscopic powder. 6-[methyl(2-morpholinoethyl)amino]-1,1-di(2-thienyl)-1-hexanol (XXIX), b.p. 1 220°, was prepd. by the method for prepn. of XXV. XXIX was converted by the methods used in the prepn. of VIII and VI into 6-[methyl(2-morpholinoethyl)amino]-1,1-di(2-thienyl)-1-hexene, b.p. 1 205° [oxalate, needles, decomp. at 192-3° (EtOH)], and N1-[6,6-di(2-thienyl)hex-5-enyl]-N1,N1,N2-trimethylethylene-1-ammonium-2-morpholinium diiodide, platelets, decomp. at 199° (EtOH). Na (20 g.) added portionwise during 30 min. to 7 g. XX in 400 cc. boiling PrOH, the mixt. boiled 2 hrs. longer, the soln. evapd. in vacuo, 500 ml. H₂O added, and the soln. extd. with Et₂O yielded on evapn. of the ext. methyl(2-pyrrolidinoethyl)[3,3-di(2-thienyl)propyl]amine (XXX), b.p. 03 160-2°; oxalate, prisms, decomp. at 200-1° (EtOH). XXX treated as in the prepn. of VI yielded N1-[3,3-di(2-thienyl)propyl]propyl-N1,N1,N2-trimethylethylene-1-ammonium-2-pyrrolidinium diiodide, needles, m. 211° (EtOH-MeOH). The following compds. were similarly prepd.: methyl(2-diethylaminoethyl)[3,3-di(2-thienyl)propyl]amine, b.p. 05 155°, from XXI; N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[3,3-di(2-thienyl)propyl]ethylene-1,2-diammonium diiodide, needles, m. 213° (EtOH); methyl(2-diethylaminoethyl)[6,6-di(2-thienyl)hexyl]amine, b.p. 05 165°, from XXVIII [oxalate, prisms, m. 149° (EtOH)]; and N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[6,6-di(2-thienyl)hexyl]ethylene-1,2-diammonium diiodide, m. 191°. The following series of compds. were prepd. by methods similar to those used in the prepn. of XVII-XIX: 5-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-pentanol, b.p. 01 162-6°; 5-[N-(2-diethylaminoethyl)-N-methylamino]-1,1-di(2-thienyl)-1-pentene, b.p. 01 170° (oxalate m. 150°); N2,N2-diethyl-N1,N1,N2-trimethyl-N1-[5,5-di(2-thienyl)pent-4-enyl]ethylene-1,2-diammonium diiodide, m. 130°; 5-[methyl(3-morpholinopropyl)amino]-1,1-di(2-thienyl)-1-pentanol, b.p. 1 215-20°; 5-[methyl(3-

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 morpholinopropyl)amino]-1,1-di(2-thienyl)-1-pentene (hydrochloride m.
 234-7'; oxalate decompd. at 212-13'); and
 N1-[5,5-di(2-thienyl)pent-4-enyl]-N1,N1N2-trimethyltrimethylene-1-ammonium-
 3-morpholinium diiodide, m. 115-17".

ACCESSION NUMBER: 1960:97715 CAPLUS
 DOCUMENT NUMBER: 54:97715
 ORIGINAL REFERENCE NO.: 54:18567b-1,18569a-1,18569a-f
 TITLE: Diquaternary compounds
 INVENTOR(S): Coker, Geoffrey G.
 PATENT ASSIGNEE(S): Wellcome Foundation Ltd.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 830519		19600316	GB	

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 AB cf. C.A. 52, 7319h. The title compound is made in an eight-step synthesis.
 Anisoiln (50 g.) 128 g. hydrated SnCl₂, 120 cc. concentrated HCl, and 125 cc.
 EtOH are heated on steam bath 2 hrs. The precipitate is filtered off and
 washed
 with dilute HCl and water to yield deoxyanisoiln (I), m. 109°. To 6.5
 g. freshly activated powdered Zn is added iodine and 15 cc. of a solution of
 12.8 g. I and 16.7 g. BrCH₂CO₂Et in 25 cc. benzene and 25 cc. toluene.
 The mixture is heated with stirring until it reacts and then cooled. The
 rest of the solution is added, the mixture heated 2 hrs., 100 cc. 10% H₂SO₄
 added, the organic layer washed with 5% H₂SO₄, 10% NaHCO₃, and water, and
 dried. The solvent is evaporated in vacuo and the residue distilled at
 280°/23 mm. to give, with dehydration during distillation, 7 g.
 Et β,γ-bis(4-methoxyphenyl)butenoate (II), m. 78°. II
 (7 g.) is saponified with 20% KOH in EtOH to yield 6 g. free acid (III), m.
 180° (EtOH); S-benzylisothiuronium salt m. 174° (EtOH).
 (III) 6 g. reduced by 300 g. 3% Na-Hg yields EtOH, 5 g.
 β,γ-bis(4-methoxyphenyl)butyric acid (IV), m. 167°.
 S-benzylisothiuronium salt m. 132° (MeOH). Dry NH₃ is passed in a
 melt of 6 g. IV at 200-30° for 1.5 hrs., the liquid poured into
 benzene and the precipitate recrystd. from EtOH to yield 4.5 g.
 β,γ-bis(4-methoxyphenyl)butyramide (V), m. 165°. V (6
 g.), suspended in 30 cc. dioxane, is added to 100 cc. cold NaOCl, prepared
 by passing Cl through 10% NaOH. The mixture is held 2 hrs. at 70-5°,
 15 g. KOH added, the mixture held 0.5 hr. at 80-5°, and cooled. 2
 hrs. The product is extracted with benzene, and the extract worked up to
 give
 2.5 g. β,γ-bis(4-methoxyphenyl) propylamine (VI), b28
 194-7°, picrate m. 224° (EtOH). To 0.8 cc. of 40%
 formaldehyde in 5 cc. EtOH is added 1.3 g. VI. The mixture is
 heated on a water bath to remove EtOH and then cooled. The Schiff base is
 obtained as a paste, and the supernatant liquid removed by decantation.
 To the Schiff base is added 7 cc. 24% HCl with stirring, and the mixture is
 heated on water bath 0.5 hr. It is evaporated to dryness, and NH₄OH is
 added.
 The precipitate is filtered off, washed with water, and recrystd. from EtOH
 to
 give 0.8 g. 4-(4-methoxybenzyl)-7-methoxy-1,2,3,4-tetrahydroisoquinoline
 (VII), m. 64°, picrate m. 264° (EtOH). VII (0.25 g.)
 treated with 10% 0.2 g. Pd-C gave 4-(4-methoxybenzyl)-7-
 methoxyisoquinoline; picrate m. 193° (EtOH).

ACCESSION NUMBER: 1959:51157 CAPLUS
 DOCUMENT NUMBER: 53:51157
 ORIGINAL REFERENCE NO.: 53:9223f-1,9224a-b
 TITLE: Syntheses of isoquinoline derivatives of
 pharmacological interest. II. Synthesis of
 4-(4-methoxybenzyl)-7-methoxyisoquinoline
 AUTHOR(S): Deshpande, V. N.; Nargund, K. S.
 CORPORATE SOURCE: Karnatak Univ., Dharwar, India
 SOURCE: Journal of the Karnatak University (1957), 2(No. 1),
 14-18
 CODEN: JKAUAR; ISSN: 0453-3348
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 GI For diagram(s), see printed CA issue.
 AB Antipyretic, analgesic N-methylsulfonates or N-
 -methylsulfonates of 1,2-dimethyl-3-phenyl-4-aminopyrazol-5-one
 are less toxic than the corresponding salts of 1-phenyl-2,3-dimethyl-4-
 aminopyrazol-5-one used hitherto and are prepared by treating compds. of
 general formula O=C.NMe.NMe.CPh:CNXR (I), where X is H and R is H, alkyl
 or aralkyl, with formaldehyde bisulfite or sulfoxalate. Instead
 of preformed H₂C(OH)SO₃Na, either HCHO and NaHSO₃ in any order or HCHO
 plus H₂SO₃ with subsequent neutralization may be used. Thus, a mixture of
 38% NaHSO₃ solution 27.4 and 30% HCHO 10 is heated to 50° and I (R = X
 = H) (II) 20.3 parts added. After total dissolution and evaporation to
 dryness
 in vacuo, the residue is crystallized from dilute EtOH giving I (R = H, X =
 CH₂SO₃Na) (III), m. 194-6°. II reacts with isopropyl bromide to
 form 1,2-dimethyl-3-phenyl-4-isopropylaminopyrazol-5-one (IV), m.
 91°. Replacing II by IV 24.5 parts in the above gives I (R =
 iso-Pr, X = CH₂SO₃Na) (V), m. 159°. Reduction of a mixture of II and
 isobutyraldehyde yields 1,2-dimethyl-3-phenyl-4-isobutylaminopyrazol-5-one
 (VI), m. 75°. Substituting VI 25.9 parts for II in the above
 produces I (R = iso-Bu, X = CH₂SO₃Na), m. 231°.
 1,2-Dimethyl-3-phenyl-4-benzylideneaminopyrazol-5-one (VII) is reduced
 catalytically to 1,2-dimethyl-3-phenyl-4-benzylaminopyrazol-5-one (VIII),
 m. 90°. Using VIII 29.3 parts instead of II in the above method
 gives I (R = PhCH₂, X = CH₂SO₃Na), m. 205°. When VII is melted
 with Me₂SO₄, water added, and the BzH formed distilled,
 1,2-dimethyl-3-phenyl-4-methylaminopyrazol-5-one (IX), m. 130°, is
 obtained. Replacing II by IX 21.7 parts in the method given leads to I
 (X, R = Me, X = CH₂SO₃Na), m. 98°. An aqueous solution of IX 21.7 is
 stirred for some time with 30% HCHO 10, and 38% NaHSO₃ solution 27.4 parts
 then added, and stirring continued at 40° for 1 hr. Evaporation and
 crystallization as above gives X, m. 98°. The NaHSO₃ solution may also be
 added to the amine first, stirring in the formalin later at
 40°. When SO₂ 6.4 is passed into a cooled solution of IX 21.7 in EtOH
 100 plus 30% alc. HCHO 10 parts and the solution stirred for a further 15
 min. and cooled, crystals of I (R = Me, X = CH₂SO₃Na) (XI) are precipitated
 and
 filtered off. XI 31.1 is added to a suspension of CaCO₃ 5 in water 100
 parts and after evolution of all the CO₂, the solution is filtered,
 concentrated in
 vacuo and the Ca salt of XI precipitated out with EtOH, decompose 304°. IX
 21.7 is added to a solution of formaldehydesulfoxalate 15.2 in water 25
 parts
 at 40-50°. The solution formed is evaporated to dryness in vacuo and
 unreacted starting material extracted with Me₂CO, leaving the I (R = Me, X =
 CH₂SO₃Na), decompose 221°. III 33.7 and Na₂CO₃ 6 are dissolved in
 water 100 and warmed with stirring to 40° with diisopropyl sulfate
 20 parts till evolution of CO₂ ceases. The solution is evaporated in vacuo
 and
 the residue crystallized from dilute EtOH, giving V, m. 159°.

ACCESSION NUMBER: 1958:113805 CAPLUS
 DOCUMENT NUMBER: 52:113805
 ORIGINAL REFERENCE NO.: 52:20200b-h
 TITLE: Salts of acid derivatives of 1,2-dimethyl-3-phenyl-4-
 aminopyrazol-5-one
 INVENTOR(S): Ehrhart, Gustav; Krohs, Walter
 PATENT ASSIGNEE(S): Farberke Hoechst AG vorm. Meister Lucius & Bruning
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1

L14 ANSWER 26 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 927992		19550523	DE	

L14 ANSWER 27 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Methyltetrahydrofurfurylamine (I) (a new substance) is claimed
 in its preparation and use as solvent of poly(vinyl chloride). The Schiff
 base
 of tetrahydrofurfurylamine with formaldehyde is
 hydrogenated (with or without solvent) at 60-80° in the presence of
 Raney Ni and 60-120 atmospheric and the mixture distilled to give 80-85% I,
 b. 152-3°. Poly(vinyl chloride) is added to I, warmed at
 45° for 1 hr., cooled to 18°, and kept 2 hrs. Data on the
 viscosity of 10-12% solns. are reported. The solns. are spun as usual,
 the coagulation bath being H₂O or, better, a 1 aqueous solution (the
 enrichment
 of I in the bath should not surpass the concentration of 75%; best
 concentration 20%).
 ACCESSION NUMBER: 1958:98023 CAPLUS
 DOCUMENT NUMBER: 52:98023
 ORIGINAL REFERENCE NO.: 52:1727h-1,1728a
 TITLE: Chemical compound for preparing viscous solutions of
 poly(vinyl chloride)
 INVENTOR(S): Siclari, Francesco; Bellano, Angelo
 PATENT ASSIGNEE(S): SNIA VISCOSA Società Nazionale Industria Applicazioni
 Viscosa S.p.A.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
IT 510118		19550120	IT	

L14 ANSWER 28 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 75°, and left 1.2 g. PhCH₂N(O)R (XVI), m. 75°, the original
 aq. acidic layer treated with 150 g. NaOH in 300 cc. H₂O and extd. 3 days
 with Et₂O yielded 73 g. RNHOH (XVII), m. 64-5° (petr. ether),
 oxidized in air to blue RNO. III (233 g.) stirred 3 days at room temp.
 with H₂SO₄ in aq. MeOH gave similarly 86 g. BzH and 120 g. (crude) R'NHCH
 (XVIII), b. 0.02 50-3°, m. 40-2° (sublimed), oxidized by air
 to R'NO. XVII (4.5 g.) and 5.3 g. BzH heated at 45°, kept 1 h. at
 50-60°, and the product isolated with 50 cc. CH₂Cl₂ gave 5.6 g.
 XVI, m. 75-6° (petr. ether). VI (8.9 g.) in 100 cc. dry MeCN
 refluxed 3 days and the resulting nitron hydrolyzed in the usual manner
 gave essentially 100% BzH and XVII. XVIII (14.5 g.) and 10.6 g. BzH
 heated 0.5 h. on the steam bath and the product isolated with 50 cc.
 CH₂Cl₂ gave 15.8 g. PhCH₂N(O)R' (XIX), m. 103-4°, hydrolyzed with
 H₂SO₄ in aq. MeOH to 100% BzH and XVIII. XVII (8.9 g.) and 4.2 g. 30% aq.
 (CHO) 2 shaken 15 min. at room temp. and the product isolated with 100 cc.
 CH₂Cl₂ gave 4.7 g. (crude) [RCN(O)CH]₂, cream-colored, m. 193-5°
 (ligroine). p-O₂NC₆H₄CHO (3.1 g.), 8.9 g. XVII, and 100 cc. C₆H₆ refluxed
 10 h. under an H₂O-separator gave 10.0 g. p-O₂NC₆H₄CH₂N(O)R, yellow, m.
 134-5° (3:1 Et₂O-petr. ether). XVIII (14.5 g.), 15.1 g.
 p-O₂NC₆H₄CHO, and 125 cc. C₆H₆ refluxed 20 h. under an H₂O-separator
 yielded 12.8 g. p-O₂NC₆H₄CH₂N(O)R', m. 119-21° (petr. ether). I
 refluxed 14 h. in 25 cc. PhMe, evapd., and chromatographed on silica gel
 gave a mixt. of p-O₂NC₆H₄CHO, an unknown material, and 2.7 g.
 p-O₂NC₆H₄CH₂N(O)CHMe₂. VI (17.7 g.) in
 50 cc. Et₂O reduced with 3.8 g. LiAlH₄ in 200 cc. Et₂O gave 14.6 g. V,
 b. 0.1 48°. VI (8.9 g.) added dropwise with stirring to 25 g. XI,
 100 cc. H₂O, 200 cc. EtOH, and 40 cc. AcOH, treated less than 15 min. with
 NaHSO₃, basified, and extd. with Et₂O gave 6.5 g. V. XVI (5.6 g.) in 50
 cc. Et₂O reduced with 1.2 g. LiAlH₄ in 200 cc. Et₂O yielded 4.3 g.
 PhCH₂NR'OH. XIX (7.5 g.) in 50 cc. Et₂O
 reduced with 1.2 g. LiAlH₄ in 200 cc. Et₂O and decompd. with HCl gave 4.5
 g. PhCH₂NR'OH (XX). HCl, m. 172-4° (EtOAc). XX.HCl and NaOH in aq.
 MeOH gave XX, noncrystallizable oil. VII (15.7 g.) in 50 cc. Et₂O reduced
 with 3.8 g. LiAlH₄ in 150 cc. Et₂O gave 10.4 g. R'NHMe, b. 19-56-8°,
 n_D 1.4305, HCl salt, m. 158-9° (EtOAc). R'NH₂CH₂ reduced with
 LiAlH₄ gave 74% R'NHMe. XI (27.6 g.) and 30.4 g. brucine N-oxide, m. 194°
 (decompn.) the filtrate washed, dried, and distd. gave 8.1 g.
 (crude) XI which fractionated yielded 4.3 g. XI, b. 0.60 60°, n_D 1.4260,
 α_D 24D -2.80° (neat). VI (35.4 g.) in 100 cc. dry C₆H₆
 treated dropwise with stirring and cooling with 20.4 g. Et₂O.BF₃ in 50 cc.
 C₆H₆, kept 1.5 h. at room temp., and filtered yielded 40 g. BF₃ salt of
 the unstable isomer (presumably cis) of XVI, m. 80-8° (CH₂Cl₂ at
 -80°), converted on recrystn. from hot EtOAc to the stable isomer
 (presumably trans) of XVI, m. 135-7°. XVI and Et₂O.BF₃ in Et₂O at
 room temp. gave an essentially quant. yield of trans-XVI. At room temp.
 cis-XVI underwent isomerization to trans-XVI. 2-Butyloxazirane (1.0 g.)
 and 5.0 g. 2,4-(O₂N)C₆H₃NNH₂ in 25 cc. concd. H₂SO₄, 36 cc. H₂O, and 125
 cc. EtOH kept overnight gave 4.2 g. mixed 2,4-dinitrophenylhydrazones of
 CH₂O and PrCHO the aq. filtrate basified and distd., the aq.
 alc. distillate shaken 1 h. at room temp. with 1.35 g. PhNCS,
 and the product isolated with CH₂Cl₂ yielded 1.2 g. PhNCSNH₂, m.
 152-4°. IX (1.4 g.) gave similarly 4.6 g. mixed
 2,4-dinitrophenylhydrazones of equal ants. of PrCHO and iso-PrCHO, and 644
 PhNCSNH₂. IV (1.0 g.) under the same conditions yielded 4.0 g.
 2,4-dinitrophenylhydrazones of equimolar ants. of CH₂O and Me₂CO, and 60%
 MeNH₂ (isolated as 1.0 g. PhNCSNHMe, m. 111-12°). X (1.9 g.) gave
 similarly 4.6 g. mixed 2,4-dinitrophenylhydrazones of equal ants. of AcH

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 cf. C.A. 51, 7343b. [Throughout this abstract R = Me₂C and R' = tert-C₈H₁₇.]
 The following imines were prepared by condensation of the appropriate
 amine with a ketone or aldehyde (b.p./mm. or m.p., and n_D20
 given): CH₂:NR, 65°/740, 1.4151; CH₂:NR', 50-2°/13, 1.4381;
 PhCH:NR, 90-2°/11, 1.5211; p-O₂NC₆H₄CH:NR, 73-5° (petr.
 ether), -, -, 6-O₂NC₆H₄CH:NR' (monocrystallizable oil), 1.5430;
 p-O₂NC₆H₄CH:NCMe₂ (I), 54-5°, -, -, p-O₂NC₆H₄CH:NCMe₂, 75-6°, -,
 iso-PrCH:NR, 51-3°/83, 1.4078; iso-PrCH:NR'BU, 67°/68, 1.4151;
 iso-PrCH:NCMePh, 68°/0.8, 1.4975; iso-BuMeC:NR, 65°/22,
 1.4272; (RN:CH₂)₂(II), 52-3°, -, BuEtCH:NR'BU, 87°/8, 1.4338;
 2-C₅H₄NCCH:NR, 56-8°/0.2, 1.5335; PhCH:NR' (III), 100°/0.4,
 1.5162; iso-PrMeC:NR, 48°/26, 1.4230; EtMeC:NCCH₂:CH₂,
 94°/100, -, Et₂C:NCMe, 52-4°/54, 1.4230; Me₂C:NCCH₃,
 53-5°/5.0, 1.4319; iso-PrCH:NCCH₂Me₂, 57°/64, 1.4097;
 Et₂C:NCMePh, 64°/0.2, 1.5050. CH₂Cl₂ (100 cc.) treated with
 stirring with 30.0 cc. 50% H₂O₂ and 2 drops H₂SO₄ and then dropwise with
 cooling during 0.5 h. with 135 g. Ac₂O, stirred 15 min. at 0° and
 30 min. at room temperature, added dropwise during 0.5 h. with stirring to
 85 g.
 CH₂:NR in 100 cc. CH₂Cl₂, kept at room temperature overnight, washed,
 dried, and
 fractionated gave 46.4 g. 2-tert-butyloxazirane (IV), b. 75-52-4°.
 n_D 1.4150, containing 93.8% active O (determined with KI and AcOH).
 PhCH:NR (V)
 (80.5 g.) in 100 cc. CH₂Cl₂ treated dropwise with stirring with 15 cc. 90%
 H₂O₂, 50 cc. CH₂Cl₂, and 1 drop H₂SO₄ at 67.2 g. Ac₂O and worked up after
 standing overnight yielded 63.1 g. 3-Ph derivative (VI) of IV, b. 0.3
 61-3°, n_D 1.5081, containing 95.6% active O. CH₂Cl₂ (100 cc.), 25.3
 cc. 90% H₂O₂, 2 drops H₂SO₄, and 114 g. Ac₂O added dropwise to 71 g. II in
 75 cc. CH₂Cl₂, kept overnight, and worked up gave 40 g. (crude)
 bis(2-tert-butyloxazirane), m. 53-6° (petr. ether at -78°),
 which chromatographed on silica gel gave material, m. 82-4°
 (presumably meso), and a 2nd fraction, m. 42-3° (presumably dl).
 Similarly were prepared the following substituted oxaziranes (substituents
 in 3, 3, and 2-positions, & yield, b.p. or m.p., mm., active O, and n_D20
 given): H, H, R' (VII), 69, 70-2°/6, 99.2, 1.4445; Ph, H, R', 67,
 -, -, 1.5019; p-O₂NC₆H₄, H, iso-Pr, 60, 46-8°, 92.0, -, p-O₂NC₆H₄,
 H, Et, 97, 34-5°, 99.3, -, p-O₂NC₆H₄, H, R, 78, 65-6°, 99.4,
 -, iso-Pr, H, R (VIII), 71, 68-70°/39, 99.8, 1.4152; iso-Pr, H, Bu
 (IX), 65, 65-7°/10, 91.5, 1.4178; BuEtCH, H, Bu, 83, -, 98.7,
 1.4350; iso-Pr, H, CMePh (X), 80, -, 99.7, 1.4956; iso-Bu, Me, Pr (XI),
 73, 61°/8, 93.6, 1.4267; p-O₂NC₆H₄, H, R', 66, 54-6°, 96.9,
 -, Me, iso-Pr, Pr, 64, 60°/15, 94.7, 1.4222; Bu, H, H, 74,
 43°/20, 98.1, 1.4178; iso-Pr, H, R', 78, -, 99.6, 1.4385; Me, Et,
 CH₂CH:CH₂, 59, 51°/6, 91.2, 1.4413; Et, Et, Et (XII), 56,
 62°/19, 97.7, 1.4225; Me, Me, CMeH₃, 14, 58°/3, 94.7,
 1.4278; iso-Pr, H, iso-Bu (XIII), 50, 53°/12, 92.0, 1.4150; Et, Et,
 MePhCH (XIV), 91, -, 90.1, 1.5038; 2-pyridyl, H, R, 75, 68-70°/0.4,
 96.1, 1.5010. CH₂Cl₂ (50 cc.), 9.8 cc. 50% H₂O₂, 1 drop H₂SO₄, and 44.1
 g. Ac₂O added with stirring to 45.9 g. N-cyclohexylideneisobutylamine
 in 50 cc. CH₂Cl₂ gave 41.1 g. 2-isobutyl-3,3-pentamethyleneoxazirane
 (XV), b. 1.5 59-62°, n_D 1.4569, containing 97.2% active O after 1 mo
 at room temperature the active O had dropped to 32% and a lower aqueous
 layer had
 separated; the organic layer (21 g.) distilled gave 5.1 g. XV, 7.5 g.
 cyclohexanone, and 3.5 g. yellow liquid, b. 0.01 68-70°, apparently a
 condensation product of cyclohexanone with 2 mol Me₂CHCH:NR. VI (177 g.)
 added dropwise with stirring and cooling to 100 cc. H₂O, 1 l. MeOH, and 60
 cc. H₂SO₄, warmed, stirred 20 h. at room temperature, poured into 1 l. H₂O,

iso-PrCH:CHCH₂CHMe₂, b47 60°.
 ACCESSION NUMBER: 1958:40503 CAPLUS
 DOCUMENT NUMBER: 52:40503
 ORIGINAL REFERENCE NO.: 52:7263d-1,7264a-1,7265a-b
 TITLE: Preparation and properties of oxaziranes
 AUTHOR(S): Emmons, Wm. D.
 CORPORATE SOURCE: Rohm & Haas, Huntsville, AL
 SOURCE: Journal of the American Chemical Society (1957), 79, 5739-54
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 52:40503

and the residue distd. give 350 g. HOCH₂Ac, b15 49-51°.
 The following compds. are similarly hydrated (amt. of starting compd. and the product, and its yield and b.p. given): MeOCH₂C.tpbond.CH, 105 g., MeOCH₂Ac, 100 g., b. 114-16°; Xib, -, MeCH(OH)Ac, no yield, b. 138-40°; (MeOCH₂C.tpbond.)₂ (XXVa), -, MeOCH₂COCH₂CH₂CH₂OMe, -, b17 83-5°; IX, 172 g., HOCH₂COCH₂CH₂CH₂OH (XXVI), 120 g., b0.6 108-10° [also prepd. in 65% yield from 500 ml. 10% aq. HOCH₂COCH₂CH₂ (XXVII) and 6 g. concd. H₂SO₄, 20-30 hrs. at 30°]; and [MeCH(OH)C.tpbond.]₂, -, MeCH(OH)COCH₂CH(OH)Me, -, b2 96-8°.
 XXIIIa (700 g.) refluxed 3 hrs. with 40% H₂SO₄ gives 280 g. 1-acetyl-1-cyclohexane, b10 73-5°. H₂O (5 g.), 2 g. BF₃-Et₂O, and 2 g. MeOH warmed to 60-70°, mixed with 64 g. MeOH, and 56 g. XX added with stirring at 50-60° so that the mixt. refluxes smoothly, cooled after a sample no longer gives a ppt. with ammoniacal XI give 55 g. 2,5-dimethyl-2,5-dimethoxy-1,4-dioxane, m. 126-8° (from MeOH); the 2,5-di-EtO analog, prepd. analogously, m. 73-4°. Aq. XX (25%) passed at 330° (80 ml./hr.) through a 1-m. long porcelain tube contg. 450 ml. catalyst (20% Cu, 1-2% Cr₂O₃ on silica gel, activated with H at 200-50°) gives 63% CH₂CHCHO. H₂C:CHAc, prepd. in 50% yield from Xib at 280-300° over 6% H₃PO₄ and 50% NaH₂PO₄ on graphite, b130 33°. XXVI, b10 45°, is prepd. in 20-g. yield (90% pure) from 5 g. H₂O, 1.5 g. Cl₃CCO₂H, 5 g. BF₃-Et₂O, and 5 g. EtOAc heated to 50-60°, cooled, added to 100 g. IX in 400 g. EtOAc, warmed to 40°, evacuated until the mixt. refluxes at 45°, and the mixt. neutralized with Na₂CO₃ and distd. when the temp. drops rapidly (about 1 hr.). This compd. polymerizes in light to a gel and, finally, to a solid, transparent, odorless, high-mol.-wt. product. XXVI (300 g.) added to 700 g. boiling Ac₂O, and refluxed 1 hr., gives 260 g. AcOCH₂COCH:CH₂, b12 81°, polymerizes to a gummy mass in a few days; 256 g. heated to 60° with 0.5 g. p-PrCH₂NHC₆H₄OH 2 days gives 240 g. 2-acetoxymethyl-6-acetoxymethyl-2,3-dihydropyran, b1 171°, m. 49°. IX (430 g.) in 700 ml. MeOH, added to catalyst mixt. prepd. by warming 15 g. H₂O, 15 g. BF₃Et₂O, and 30 ml. MeOH, the temp. held to 30° by cooling, warmed a short time with 500 ml. 1% H₂SO₄ after reaction heat has died away, neutralized with Na₂CO₃, filtered, and distd. gives MeOCH₂CH₂COCH₂OH (XXVIII), b7 84-7°. Sapp. H₂O from the soln., distg. the excess MeOH, and cooling the mixt. gives 2,5-dimethoxy-2,5-bis(β-methoxyethyl)-1,4-dioxane, m. 82°; this hydrolyzes to XXVIII on warming with dil. H₂SO₄. EtOCH₂CH₂COCH₂OH, b16 104-6°, and iso-PrCH₂CH₂COCH₂OH, b5 94°, are prepd. analogously. H₂SO₄ (35 g.) and 125 g. 50% HOCH₂C.tpbond.CCH₂MeOH treated at 60° and 130 mm. with an addnl. 375 g. of the diol gives 60 g. CH₂:CHCOCH₂CH₂OH (or MeCH:CHCOCH₂OH), b18 75° [MeCH(OH)C.tpbond.]₂ (200 g.) in 800 ml. H₂O mixed with 10 g. H₂SO₄ in 60 g. 17% H₂SO₄ at 30-5° (with cooling) gives 140 g. MeCH:CHCOCH₂MeOH, b2 48°. Hydrogenation of the corresponding oxo alcs. or glycols over Raney Ni at 200 atm. and 25-120° gives the following compds. in good yield: [MeCH(OH)]₂ (XXVIIIa), b. 179°; HOCH₂CH₂EtOH, b. 191°, b10 96-7°, from XXVII (40% soln. of XXVI (prepd. from 500 g. 33% aq. IX, 5 g. H₂SO₄, and 10 g. concd. H₂SO₄ at 30°) adjusted to pH 5 with Ca(OH)₂ and the ppt. filtered off and hydrogenated at 150° and 100 atm. gives 120 g. XXVIIIa; diacetate, b20 85-90°; HOCH₂CH₂(OH)CH₂CH₂OH, b1 130-1° (cyclic formaldehyde acetal, C₅H₁₀O₃, prepd. with (CH₂O)_n and FeCl₃, b. 198-9°, b0.1 67-8°). The following HOCH₂CH₂(OH)CH₂CH₂OH are similarly prepd. from the 2-oxo precursor (R given): Me, b12 116°; Et, b10 122°; iso-Pr, b10 126-7°; tert-Bu, b4 110-11°. [MeCH(OH)C.tpbond.]₂ (400 g.) and 600 ml. H₂O stirred and treated at 70-80° during 40 min. with 40 g. H₂SO₄, neutralized

AB Hydrogenation to unsatd. and saturated alcs. and glycols, hydration, addition of
 HCl and NaHSO₃, oxidation of Via to (HOCH₂R₃4C.tpbond.C)₂ (XXIIIC), esterification and etherification, and the preparation of amino- and haloalkynes are discussed. A selective catalyst (XXIV) for hydrogenation of Via to cyclic alcs. is prepared by vacuum impregnating 1 kg. granular kieselguhr with solns. of 0.65 g. PdCl₂ and of 13 g. FeCl₃ each in 400 ml. H₂O, drying, boiling 1 l. 0.5 hr. with 500 ml. concentrated water glass solution and 2.5 l. H₂O, filtering (vacuum) after 12 hrs., drying at 100°, and reducing with H at 140-50°. XXIV contains 1.5% free alkali. Distillation of 500 g. condensate from passing 25% aqueous XX and H over XXIV at 140-50° gives a little EtCHO, a mixture (b. 80-92°) containing 110 g. CH₂:CHCH₂OH, 12 g. PrCHO with 12% H₂O, and a trace of XX. Similarly prepared from the corresponding Via are: CH₂:CHCH(OH)Me, b. 97° (azeotrope containing 26% H₂O, b. 85-6°); Me₂C(OH)CH:CH₂, b. 99°; CH₂:CHCMe(OH)Et, b. 118°; and 1-vinyl-1-cyclohexanol, b2077°, m. 4°. These compds. can also be prepared with Fe powder (prepared from Fe carbonyl) as catalyst at 50°, 100 atmospheric H, reduction being stopped when the calculated amount of H has reacted. XXIII (200 g.), hydrogenated at room temperature and 50 atmospheric over 5 g. Raney Ni until half the calculated amount of H has reacted, then at 80° and 200 atmospheric to complete reaction gives 185 g. Me₂C(OH)Et, b. 102°. PrOH, sec-BuOH, MeEt₂COH, b. 124°, and 1-ethyl-1-cyclohexanol, b40 93°, are prepared similarly. Catalyst for preparing aldehydes and ketones from acetylenic alcs. is prepared from 500 g. kieselguhr containing 3% Fe, and 0.6% S (as SO₄--), made into a paste with 5 g. PdCl₂.2H₂O in 200 ml. H₂O, dried, powdered, pelleted, and reduced with H at 200°. XX (35 g.) and 15 g. H₂O are vaporized over 100 ml. of this catalyst at 105° and 40 l. H for 1 hr. Distillation of 500 g. of condensate gives 300 g. EtCHO. MeCOEt is prepared similarly from Xib. Crude IX from 30% VIII, 1.5 kg., hydrogenated over 50 g. Raney Ni (or other common hydrogenation catalysts) at 40-60° and 200 atmospheric (with cooling to control reaction) gives 500 g. (CH₂CH₂OH)₂, m. 20.1°, b. 229, b0.7 106°, d20 1.069, nD20 1.4461, bis-urethane, m. 198-200°. HOCH₂CH₂CH₂CH₂CH(OH)Me, b15 125-8°, [MeCH(OH)CH₂]₂, b18 132-3°, b0.4 95-100° (diacetate, b15 114°), [Me₂C(OH)CH₂]₂, b15 117-18°, b15 117-18° (from EtOAc), and 1,1'-ethylenedicyclohexanol, b2 145°, m. 128-30°, are also prepared in similar yields. (CH₂CH₂OH)₂ (180 g.) heated 4 hrs. with 5 g. FeCl₃ and 60 g. (CH₂O)_n (or 30-40% VIII) gives 184 g. acetal, b. 117°. IX (500 g. 33%), and 50 g. Fe (prepared from Fe carbonyl), treated at 50° with 100 atmospheric H and reaction stopped when the calculated amount of H has reacted give 150 g. (HOCH₂CH₂)₂ (XXV), b. 237-9°, b3 116-21°, m. 4°, diacetate, b13 108-10°, b13 108-10°. Other suitable catalysts for aldehyde acetal, b. 124°. CH₂:CHCHO and suitable catalysts are Co, poisoned by adding 0.1% KSCN to the solution, and 0.2% Et-C treated with 0.15% Na₂HPO₄, 0.1% H₃BO₄, or 1.5% C₅H₅N. Partial hydrogenation is also obtained with H containing 3-5% CO. [MeCH(OH)CH₂]₂, b6 109-11°, [Me₂C(OH)CH₂]₂, b20 120-2°, m. 77°, and 1,1'-vinylendicyclohexanol, m. 154°, are prepared similarly in nearly quant. yield. XX hydrated by heating 1500 g. 30% aqueous solution with 50 g. H₂SO₄ and 5 g. concentrated H₂SO₄ to 70° until the carbonyl number is constant, the mixture neutralized, the H₂O azeotroped off with CH₂Cl₂ or XIIa,

and 2% Na₂CO₃, after 20 min. with dil. H₂SO₄ acidified with dil. H₂SO₄ neutralized with CaCO₃, filtered off, and hydrogenated at 100° and 200 atm. over 200 g. "nickel-chromium oxide" catalyst, give 150 g. Me[CH(OH)]₂Pr, b0.7-0.8 102° (gives deep blue color with CuSO₄-NaOH), and a little Me[CH(OH)]₂CH₂CHMeOH, b0.7 140-50°. HOCH₂CH₂EtOH (50 g.) and 5 g. p-MeC₆H₄SO₃H (or KHSO₄) heated rapidly to 160° with removal of H₂O give 4 g. PrCHO and 25 g. 2,5-diethyldioxane, b21 62°, 50 g. XXVIIIa and 6 g. of a mixt. of equal parts of p-MeC₆H₄SO₃H and KHSO₄ give 65 g. 2,3,5,6-tetramethyl-1,4-dioxane, b. 138-9°. HOCH₂CH₂(OH)CH₂CH₂OH gives 0.8 2,5-bis(β-hydroxyethyl)dioxane, b20 90°. Xib (125 g., 60%) is added during 5 hrs. to 500 ml. of a distg. soln. contg. 3.8% FeSO₄, 41.4% Fe₂(SO₄)₃, 0.15% H₂SO₄, and 1.2% H₂SO₄ (the original vol. maintained by adding H₂O) and the distillate satd. with NaCl and redistd. gives 20 g. Ac₂, b. 87-8°. [MeCH(OH)C.tpbond.]₂ (300 g.) refluxed with 143 g. 80% H₃PO₄, 1.5 g. H₂SO₄, and 1 l. H₂O, gives 260 g. AcCOPr, b150 82-5°, dioxime, m. 173°, dioxime-nickel complex, orange-red, m. 158-60°, and as by-product, 2,5-dimethyl-3-oxetetrhydrofuran, b150 94-5° (semicarbazone, m. 168-71°). HOCH₂CH₂(OH)Et passed at 180° over granular CuO is converted in 32% yield to a mixt. contg. about 45% EtCOCHO (XXIX) and HOCH₂COEt. IX (200 g.), 40 g. HgCl₂, and 400 g. (CH₂OH)₂ heated 4 hrs. at 185° give 160 g. XXIX diethylene glycol acetal (C₈H₁₄O₄), b12 100-5°, which partly crystall. on standing; 100 g. of this and 500 ml. 1% H₂SO₄ stirred 9 hrs. at 90° give XXIX, which polymerizes rapidly (dioxime, m. 129°), and XXIX monethylene glycol acetal, b12 90-5°. XXVI (104 g.) and 300 ml. 30% VIIJ added at 70-80° to 500 g. CuSO₄ in 2 l. H₂O and 2 kg. 20% NH₃, held at 70-85° 1-2 hrs., and the Cu complex filtered off, suspended in H₂O, decompd. with H₂S, and the aq. soln. distd. give (2-hydroxyethyl)imidazole, b1 170-5° (picrate, m. 144°); this with SOCl₂ gives (β-chloroethyl)imidazole which with alc. NH₃ gives histamine di-HCl, m. 236-8° (picrate, m. 144°). IX (60 g.) heated 13 hrs. with 150 g. MeOH and 3 g. ZnCO₃, gives EtCH(OH)CO₂Me, b30 68°; other esters of this acid prepd. similarly are: Et, b. 167-9°, Bu, b. 200-2°, allyl, b20 85-8°, PhCH₂, b33 170-5°, and cyclohexyl, b37 145-50°. HCl passed into 112 g. XX and 6 g. HgCl₂ heated to 60°, the soln. neutralized with alkali when the temp. falls to 70° after reaction ceases, and satd. with K₂CO₃ gives 140 g. CH₂:CClCH₂OH, b. 135-40°; also prepd. (225 g. from 500 g. 30% aq. XX, provided HCl addn. is rapid and temp. held to 80°). XX (60 g.), 100 g. NaHSO₃, and 100 ml. H₂O refluxed several hrs., cooled, filtered, and dil. with MeOH gives NaO₃SCH₂CH₂CH₂CH₂OH; analogously, XXIII gives NaO₃SCH₂CH₂(SO₃Na)CH₂OH and 20 g. IX give 260 g. HOCH₂(CHSO₃Na)₂CH₂OH. Aq. XX (39 ml. 27.16%), 85 ml. H₂O, 9 g. XI, and 25 g. NH₄Cl shaken with O at 0° give 9.6 g. (HOCH₂C.tpbond.C)₂, m. 111-12° (from Et₂O-petr. ether) (also prepd. in quant. yield by a continuous process), which hydrogenates in MeOH over Raney Ni at 60° and 200 atm. to give 1,6-hexanediol, m. 41.5°, b13 143°. Other RC.tpbond.CH oxidized similarly in quant. yield to (RC.tpbond.C)₂ are (R and product const.): MeCHOH, m. 69-90° (mixt. of stereoisomers, m. 68° and 109° resp.); CH₂:CH, b3 40°; and HOCH₂CH₂CH₂, decomp. above 220°. A mixt. of 60 g. H₂C:CHC.tpbond.CH and 70 g. XXIII gives HOCH₂Me₂C.tpbond.CC.tpbond.CCH₂CH₂, b3 75°. XX (9 ml. 97.5%) added to 35 g. Cu(OAc)₂.2H₂O and 30 g. NH₄Cl in 90 ml. H₂O (boiled in N) pptd. greenish yellow C₃H₃OCu₂Cl. The following esters of XX are prepd. by conventional methods: acetate, b. 110-12°; carbonate (C₇H₆O₃) (from COCl₂), b20 97°; adipate (C₁₂H₁₄O₄), b4 142-5°; benzoate, b5 102-7°; p-nitrobenzoate, m.

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88-90° (from ligroine); benzenesulfonate (XXXI), b2 140-2°; and p-toluenesulfonate (XXXII), b5 161-2°. Also prep'd. is HC.tplbond.CCH(OAc)Et, b. 139-40°. XIB esters prep'd. are: acetate, b. 124-6°; benzoate, m. 27-9° (from ligroine); and p-toluenesulfonate, m. 58-60° (from cyclohexane). Also prep'd. is (AcOCH2C.tplbond.)2, b3 106°. Me2SO4 (75 g.) added at 40° to 56 g. XX in 44 ml. H2O and 110 g. 50% NaOH so that the temp. stays below 60°, stirred 2 hrs. at 50-60°, and distd. gives 62 g. MeOCH2C.tplbond.CH, b. 65°. Ethylene oxide (45 g.) and 58 g. 96% XX added rapidly and simultaneously to 300 ml. 2% NaOH and neutralized after 1 hr. give 41 g. HOCH2(CH2OCH2)2C.tplbond.CH, b12 76-7°, b14.5 79-80°. CH2:CHCN (53 g.) added to 60 g. 94% XX (dried over K2CO3 just before use) and 0.5 g. powd. NaOH, the temp. allowed to rise to 100°, then held at 50° for 1 hr. with cooling, neutralized with dil. H2SO4 and distd. gives 75 g. HC.tplbond.CCH2OCH2CH2CN, b13 101-2°. PhOH (200 g.), 500 g. XXX, 315 ml. 35% NaOH, and 1.5 l. H2O stirred 2 hrs., heated to 90-5°, poured onto ice, and extd. with Et2O give 200 g. HC.tplbond.CCH2OCH2CH2CN. Other HC.tplbond.CCH2OCH2CH2CN prep'd. similarly using XXX or XXXI are (R and m.p. or b.p.): o-O2NC6H4, m. 78-9° (from MeOH); p-O2NC6H4, m. 118-20°; o-OCH3C6H4, m. 72-4° (from ligroine); pyrocatechol, b13 121-4°; β-naphthyl, m. 64-6° (from MeOH). Crude XXX (670 g.) and 250 ml. 35% NaOH added in 4 portions to 250 g. o-HOC6H4NHAc in 1570 ml. H2O, the mixt. heated 1 hr. to 90°, treated with 30 ml. NaOH, cooled, and extd. with Et2O, the ext. washed with 15% HCl, then 5% NaOH, and evapd., and the residue heated 1 hr. with 1 l. 1:1 HCl give 81 g. o-HC.tplbond.CCH2OCH2CH2CN. Similarly, p-HOC6H4CO2Me gives p-HC.tplbond.CCH2OCH2CH2CN, m. 212-14° (from MeOH) 40 g. XXX gave 10 g. p-HC.tplbond.CCH2OCH2CH2CN, m. 109-11°; hydrolysis gives the amine, b4 118-20°, from which an azo dye is prep'd. by diazotization and coupling with 1-phenyl-3-methyl-5-pyrazolone. (XXVa) b14 58°, is prep'd. in 400 g. yield by adding 1350 g. Me2SO4 and 1075 g. 40% NaOH to 400 g. IX in 400 ml. H2O at 40° so that the temp. remains const. without heating, stirring 2 hrs. at 50-60°, sepg. layers, treating the lower layer with another 600 g. Me2SO4 and 475 g. 40% KOH, and distg. the org. layers. Similarly 72 g. XXXIII gives 65 g. (Me2C(OMe)C.tplbond.)2 (XXXII), b19 86-8°. Heating 172 g. 50% IX and 400 g. 50% NaOH to 80°, adding 250 g. MeHSO4 during 1 hr., stirring 4 hrs., and extg. with Et2O, gives 26 g. HOCH2C.tplbond.CCH2OCH2CH2CN, b30 106°, and 24 g. XXVa. Freshly distd. PhNH2 (93 g.) and 196 g. XXX mixed in an ice bath (temp. rises to 120°), the soln. cooled, 100 ml. Me2CO added, the crystals washed with Me2CO, the combined filtrate and washings steam distd., the distillate extd. with Et2O, the ext. dried and distd., the base (b28 146-52°) (37 g.) dild. with 50 ml. C6H6, refluxed 1 hr. with 25 ml. Ac2O, and extd. with HCl, and the ext. neutralized give 11 g. PhN(CH2C.tplbond.CH)2, b4 94-6°. PhNHR2 prep'd. similarly, using XXXI or the benzene-sulfonate of XIB, are (R1 and R2 given): Me, CH2C.tplbond.CH, b4 80-3°, m. 35-6°; Me, CHMeC.tplbond.CH, b1 76-8°, CH2C.tplbond.CH, CH2C.tplbond.CH, b2 135-7°, and CH2CH2OCH2, CHMeC.tplbond.CH, b3 137-40°. IX (344 g.) treated during 10 min. with 1200 g. SOCl2, left overnight at 10-15°, warmed to 80°, SOCl2 removed at the H2O pump, and the residue distd. gives 370 g. (ClCH2C.tplbond.)2 (XXXIII), b16 65-6° (reagents in this prep'n. must be freshly distd. and the distn. residue must not be heated above 100° or an explosion may occur). (Me2CClC.tplbond.)2, prep'd. similarly, b11 60-70°. IX (344 g.), and 476 g. SOCl2 as above gives a lava-like mass which, crystd. from Ac2O or HOCH2Me2, gives the cyclic disulfite

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AB The following N,N-disubstituted 3-hydroxydimethylamines are prepared by heating 3-hydroxypyridine and the resp. amine in H2O or EtOH with a 30% formalin solution for 2 hrs. and distilling the product: di-Me (I), b0.3 60°, m. 56-9°; di-Et (II), b2.7-3.7 90-110°; di-Bu (III), b1.3 110-20°; methylbenzyl (IV), b1.3 126-35°. Also 1-(3-hydroxy-2-pyridylmethyl)piperidine (V), b0.8 95-7°. I is converted to the methobromide (VI), m. 175-7°, with MeBr and the di-HCl salt (VII), m. 178-86°, with alc. HCl. The following carbamates are prepared by warming the resp. 3-hydroxy-2-pyridylmethylamine in pyridine or C6H6 with Me2NCOCl, allowing the mixture to stand at room temperature for 16 hrs., removing the solvent, and treating the residue with anhydrous HCl, yielding HCl salts. Dimethylcarbamate of I, HCl, m. 128-30°; I, 2HCl, m. 163-7°; II, 2HCl, m. 117-19°; IV, 2HCl (VIII), m. 167-9°; V, 2HCl, m. 111-25°. With MeBr instead of anhydrous HCl above are obtained the dimethyl carbamates of I, MeBr, m. 175-7°; III, MeBr, m. 154-5°; V, MeBr, m. 156-7°; II, MeBr, m. 141-3°. By substitution of the respective carbamyl chloride for Me2NCOCl, the following di-substituted carbamates of I, MeBr are obtained: (p-bromophenyl)methyl, m. 176-8°; methyl-p-tolyl, m. 153-5°; diiso-Pr, m. 173-5°. Similarly the carbamate of I, m. 91.5-4.5°, and the N-methylcarbamate of II, HCl, m. 142-4°, are prepared VIII yields on reduction with H and PdCl2 on charcoal the dimethylcarbamate of 3-hydroxy-N-methyl-2-pyridylmethylamine-ZHCl, m. 140-1°. To 15 g. 3-hydroxypyridine and 30 g. PhNHCH2CH2NET2 in 100 cc. of 70% EtOH is added 13.5 cc. of 35% formaldehyde solution, the mixture refluxed for 2 hrs., the solvent removed, and the residue treated with dilute HCl, yielding N,N-diethyl-N'-phenyl-N'-(3-hydroxy-2-pyridylmethyl)ethylenediamine-HCl (IX), m. 199-200°; the free base can be methylated with CH3NH2 and then treated with dilute HCl, yielding N,N-diethyl-N'-phenyl-N'-(3-methoxy-2-pyridylmethyl)ethylenediamine-ZHCl, m. 72-4°. The free base of IX treated with Me2NCOCl and then with MeBr gives the dimethylcarbamate of N,N-diethyl-N'-(2-(N'-(3-hydroxy-2-pyridylmethyl)-N'-phenylamino)ethyl)-N-methylammonium bromide, m. 172-3.5°. 3-Hydroxypyridine and Et2NCH2CH2NHCCH2Ph and 35% HCHO solution in 70% EtOH yield N,N-diethyl-N'-benzyl-N'-(3-hydroxy-2-pyridylmethyl)ethylenediamine-ZHCl, m. 180-1°.

ACCESSION NUMBER: 1950:46950 CAPLUS
DOCUMENT NUMBER: 44:46950
ORIGINAL REFERENCE NO.: 44:8961h-1,8962a-e
TITLE: Carbamic acid esters of 3-hydroxy-2-pyridylmethylamines
INVENTOR(S): Aeschlimann, John A.; Stempel, Arthur
PATENT ASSIGNEE(S): Hoffmann-La Roche Inc.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2512732		19500627	US	

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(CH8O6S2) (XXXIV), colorless crystals, m. 196-7°, of IX; IX is recovered in 8.4-g. yield by heating 25 g. XXXIV 0.5 hr. with 100 ml. 30% NaOH. Adding 57 g. 40% aq. NaOH at 75° to 12.3 g. XXXIII in 50 ml. EtOH gives 1.9 l. (HC.tplbond.C)2. XXXIII (123 g.) treated with 430 g. pyrrolidone 2 hrs. at 20° gives 170 g. 1,1'-(2-butynylene)dipyrrolidone, b2.5 116-16.5°, 1,4-dipiperidino deriv. (70 g. from 62 g. XXXIII and 180 g. piperidine) b5 160-1°.
ACCESSION NUMBER: 1956:89208 CAPLUS
DOCUMENT NUMBER: 50:89208
ORIGINAL REFERENCE NO.: 50:16774b-1,16775a-1,16776a-1,16777a-d
TITLE: Ethynylation. IV. Reactions of α-alkynols and γ-alkynediols
AUTHOR(S): Reppe, Walter; et al.
SOURCE: Ann. (1955), 596, 38-79
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 50:89208

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AB Iso-PrNH2 (118 g., 2 mol) at 17-20°, treated with 2 mol of 36% aqueous HCHO and then with 2 mol of Me2CHNO2 with stirring for 30 min., 20 g. Na2SO4 added, and the nonaq. layer allowed to stand at room temperature for 5 days and distilled, gives 76% of N-(2-nitroisobutyl)-isopropylamine (I), b10 84°, nd20 1.4339, d2020 0.9685 (all n and d. under these conditions). Iso-PrNH2 (59 g.) and 119 g. Me2C(NO2)CH2OH, shaken and allowed to stand 3 days at room temperature, gives 86% of I. Iso-PrNH2 (2 mol) and 2 mol 30% aqueous HCHO, treated during 30 min. with 1 mol of EtNO2, give 71% of 2-nitro-2-methyl-1,3-diisopropylaminopropane (II), b3 98-100°, n. 1.4518, d. 0.9671. II results also in 60% yield from 2 mol of iso-PrNH2 and 1 mol of O2NCMe(CH2OH)2 on standing at room temperature for 3 days. The following were similarly prepared by using HCHO and the other reactants named: N-(2-nitroisobutyl)methylamine (MeNH2 and Me2CHNO2), 48%, b6 60-2°, n. 1.4368, d. 1.0166; N-(2-nitro-2-methylbutyl)isopropylamine (iso-PrNH2 and 2-nitrobutane), 90%, b10 95-7°, n. 1.4409, d. 0.9625; N-(2-nitroisobutyl)butylamine (BuNH2 and Me2CHNO2), 85%, b10 105-7°, n. 1.4407, d. 0.9584; N-(2-nitroisobutyl)-1-methylpropylamine (EtMe-CNH2 and Me2CHNO2), 72%, b10 96°, n. 1.4384, d. 0.9571; N-(2-nitroisobutyl)benzylamine (PhCH2NH2 and Me2CHNO2), 75%, b2 130-3°, n. 1.5178, d. 1.0785; 2-nitro-2-chloro-1,3-dibenzylaminopropane (PhCH2NH2 and ClCH2NO2), 80%, m. 74.9°; N-(2-nitroisobutyl)-2-phenylethylamine (MePhCH2NH2 and Me2CHNO2), b0.8 121-4°, n. 1.5080, d. 1.0809; N-(2-nitroisobutyl)-2-amino-2-methyl-1-propanol (Me2C(NH2)CH2OH and Me2CHNO2), 90%, m. 59°; N-(2-nitroisobutyl)-2-amino-1-butanol (EtCH(NH2)CH2OH and Me2CHNO2), 10%, m. 58.1°. The nitro amines (100 g.) in 100 ml. MeOH were reduced over 5 g. Raney Ni at 30-50° and 500 lb./sq. in. H pressure, the MeOH being removed at atmospheric pressure and the H2O by distillation with C6H6; the same yields were obtained with crude or pure nitro amines (on the basis of the nitro paraffins). N-(2-Aminoisobutyl)methylamine, b750 123°, n. 1.4293, d. 0.9149; 2-amino-2-methyl-1,3-diisopropylaminopropane, b3 98-100°, n. 1.4502, d. 0.8596; N-(2-aminoisobutyl)isopropylamine, b760 147.3°, n. 1.4263, d. 0.8025; 2-amino-2-ethyl-1,3-diisopropylaminopropane, b1 71-2°, n. 1.4491, d. 0.8520; N-(2-aminoisobutyl)butylamine, b10 64-6°, n. 1.4346, d. 0.8154; N-(2-aminoisobutyl)-1-methylpropylamine, b10 56-8°, n. 1.4297, d. 0.8171; N-(2-amino-2-methylbutyl)isopropylamine, b10 57.5°, n. 1.4348, d. 0.8166; N-(2-aminoisobutyl)benzylamine, b8 105-6°, n. 1.5153, d. 0.9526; N-(2-aminoisobutyl)-1-phenylethylamine, b5 110°, d. 0.9373; N-(2-aminoisobutyl)-2-amino-2-methylpropanol, b10 115-16°, n. 1.4651, d. 0.9360; N-(2-aminoisobutyl)-2-aminobutanol, b10 118-21°, n. 1.4631, d. 0.9343.

ACCESSION NUMBER: 1946:8259 CAPLUS
DOCUMENT NUMBER: 40:8259
ORIGINAL REFERENCE NO.: 40:1444a-h
TITLE: Reaction of primary aliphatic amines with formaldehyde and nitro paraffins
AUTHOR(S): Senkus, Murray
CORPORATE SOURCE: Commercial Solvents Corp., Terre Haute, IN
SOURCE: Journal of the American Chemical Society (1946), 68, 10-12
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal

LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 40:8259

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AB Cyclohexanone (50 g.), 95 g. PhNH₂, 88 cc. concentrated HCl and 13 cc. EtOH.

warmed 4 days on the H₂O bath, give 53 g. PhNH₂, 1.5 g. cyclohexenylaniline (I) and 70 g. di-aminodiphenylcyclohexane (II); if the condensation is continued for 12 days, there result 35 g. PhNH₂, 2.3 g I and 99 g. II. I pale yellow, b₁₄ 175°, HCl salt, m. 228°; Picrate, m. 170°; Ac compound, m. 152°; Bz compound, m. 177°; phenylthiourea, m. 144°; benzal compound, m. 82°. Reduction gives p-cyclohexylaniline, m. 45°; warming I with PhNH₂ in HCl or better with PhNH₂.HCl gives II. I, b_{0.1} 248°, m. 114°; HCl salt, m. 235°; Ac compound, m. 266°; diphenylthiourea, m. 163°. Warming 114 g. II, 78 cc. concentrated HCl and H cc. EtOH 12 days at 100° gives 5 g. PhNH₂, 8 g. I and 96 g. II. A slight decomposition of II takes place upon heating at 305°; a little HCl, H₂SO₄, HBr or ZnCl₂ causes a more marked decompn.; H₃PO₄ or Cl₃CCO₂H has no action. PhNHMe (107 g.) and cyclohexanone (50 g.), heated 12 days as above, give 123 g. 1,1-di(methyl-amino)diphenylcyclohexane, b_{0.3} 250-2°, m. 124° (HCl salt, m. 220°; picrate, m. 105°; di-Ac derivative, m. 185°; diphenylthiourea, m. 166°) and 3.5 g. *N*-methylcyclohexenylaniline, b₁₄ 184° (HCl salt, m. 212°; picrate, m. 114°; Ac derivative, m. 85°; N-NO compound, m. 80°). PhNHMe₂ (123 g.) and 50 g. cyclohexanone give 125 g. di(dimethylamino)diphenylcyclohexane, b₁₂ 282-3°, m. 164° (HCl salt, m. 180°; picrate, m. 148°; dimethiodide, m. 178°) and 4.5 g. cyclohexenyldimethylaniline (III). b₁₄ 190°, m. 56° (HCl salt, m. 195°; picrate, m. 162°; methiodide, m. 190°). 1,1-Amino(dimethylamino)diphenylcyclohexane, light yellow, b_{0.3} 250-5°, m. 101° (HCl salt, m. 115°); distillation with a couple drops of dilute HCl gives PhNHMe₂ and I. 1,1-Dimethylaminophenyl[diethylaminophenyl]cyclohexane, b_{0.1} 260-5°, m. 108° (HCl salt, m. 141-2°, strongly hygroscopic). Condensation with α -ClOH₇NH₂ is slow, the yield being only 13% after 90 hrs.; the compound, C₂₄H₂₃N₂, b_{0.1} 270-80°, m. 152°. III in fuming HBr gives the Compound C₁₄H₂₃NBr, m. 95° (20% yield) (picrate, m. 152°). Cyclohexanone (20 g.) and 50 g. tetrahydroquinoline give 5 g. 6-cyclohexenyltetrahydroquinoline, b_{0.1} 163-5° (HCl salt, m. 120°; picrate, m. 90°) and 30 g. 1,1-di(tetrahydroquinolyl)cyclohexane, b_{0.1} 265-7° m. 114° (di-NO compound, m. 85°; di-Bz derivative, m. 154°; diphenylthiourea, m. 92°). m-MeC₆H₄NH₂ gives only a few % of 3-methyl-4,6-dicyclohexenylaniline, yellow oil, b₁₂ 230-5° (picrate, m. 176-7°); p-MeC₆H₄NH₂ (110 g.) gives 9 g. of 4-methyl-2,6-dicyclohexenylaniline, b₁₃ 228°, m. 60° (picrate, m. 192°; Bz compound, m. 69°). p-Cyclohexylaniline (30 g.) gives about 1 g. of the compound C₂₄H₂₅N, b₁ 200-5°. 3-Methylcyclohexanone (IV) (50 g.) and 83 g. PhNH₂ after 12 days at 100° give 42 g. PhNH₂, 24 g. methylcyclohexenylaniline (V), b₁₄ 187-90° (Ac derivative, m. 127°; Bz derivative, m. 178°; phenylthiourea, m. 143°), and 38 g. 1,1-diaminodiphenyl-3-methylcyclohexane (VI). b₁₄ 285-90° (HCl salt, m. 214°; diphenylthiourea, m. 127°); 40 g. PhNH₂ and 80 g. IV, 12 days at 100°, give 14 g. PhNH₂, 27 g. V and 74 g. VI. PhNHMe₂ (100 g.) and 100 g. IV give 28 g. methylcyclohexenyldimethylaniline, b₁₄ 194-6°, m. 38° (picrate, m. 162°; methiodide, m. 159°), and 11 g. 1,1-tetramethyldiaminodiphenyl-3-methylcyclohexane, b₁₂ 295°, m. 109° (picrate, orange, m. 164°; dimethiodide, m. 186°). o-Methyl-cyclohexanone condenses more slowly than IV and yields probably 2-methylcyclohexenylaniline, b₁₄ 160°

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AB To gain an insight into the course of the reaction of phenols and amines or amides with HCHO, as well as the hardening of such mixed condensates, model expts. have been carried out. 2,4,6-Me₂(HOCH₂)C₆H₂OH (I) (3 g.), 5.4 g. NH₂CO₂Et and 10 g. K₂S₂O₈, heated at 55° for 18 hrs., give N-(2-hydroxy-3,5-dimethylbenzyl)ethylurethan (II), m. 67°. Attempts to condense I with AcNH₂ or BzNH₂ failed in acid or alkaline solution because the hydrolysis of the amide was more rapid than the condensation. With K₂S₂O₈ at 65°, I and AcNH₂ give CH₂(NHAc)₂ and CH₂(C₆H₂Me₂OH-3,5,2) (III); likewise, BzNH₂ yielded CH₂(NHBz)₂ and III; the intermediate in this reaction is assumed to be the ether (IV), [Me₂(OH)C₆H₂CH₂]₂O. I is unchanged on heating at 65° for 18 hrs. but with K₂S₂O₈ it gives a good yield of III; IV is unchanged on heating at 105° for 10 hrs. but with K₂S₂O₈ it also gives III. The condensation product of I and CO(NH₂)₂ [2,4,6-Me₂(H₂NCONHCH₂)C₆H₂OH] (V) (3.5 g.), 3 ml. 40% HCHO and 200 ml. saturated Ba(OH)₂, allowed to stand overnight, give N1-methylol-N2-(2-hydroxy-3,5-dimethylbenzyl)urea, Me₂(OH)C₆H₂CH₂NHCONHCH₂OH, m. 162°. V (4 g.) in 200 ml. 50% MeOH, 5 ml. 40% HCHO and 15 ml. 2 N NaOH, allowed to stand overnight, yield N1,N1-methylenebis(N2-2-hydroxy-3,5-dimethylbenzylurea) (VI), CH₂(NHCONHCH₂C₆H₂Me₂OH)₂, m. about 200° (decomposition). Distn. of V at 12 mm. gives 6,8-dimethyl-3,4-dihydrocoumaraz-2-one (VII), m. 182.5°; it also results by heating II at 300° or from the *N*-Me derivative of V at 12 mm. It is believed that the formation of VII does not play a role in the hardening of resins. Although the lactone bridge in VII is not cleaved by concentrated H₂SO₄ in EtOH, 2 N NaOH gives a mol. compound, m. 101-15° (decomposition), of Me₂(HO₂CNHCH₂)C₆H₂OH and 2-hydroxy-3,5-dimethylbenzylamine (VIII); this was cleaved by boiling with CSH₅N and VIII was purified through the HCl salt (m. p. of VIII not given).
ACCESSION NUMBER: 1944:18455 CAPLUS
DOCUMENT NUMBER: 38:18455
ORIGINAL REFERENCE NO.: 38:2648f-1,2649a
TITLE: Phenol-urea condensation products and the formation of coumarazones
AUTHOR(S): Nystrom, Holger
SOURCE: Kunststoff-Tech. u. Kunststoff-Anwend. (1942), 12, 81-4
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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(chloroplatinate, m. 211-2°). Cyclopentanone (20 g.) and 86 g. Ph-NMe₂ heated with concd. HCl 10 hrs. at 150° give 20 g. cyclopentenylidimethylaniline (VII), b₁₂ 160°, m. 10° (HCl salt, m. 170°; picrate, m. 129°; methiodide, decomp. 180°), and 12 g. 1,1-tetramethyldiaminodiphenylcyclopentane, m. 128° (HCl salt, m. 213°; picrate, m. 181°; dimethiodide, decomp. 195°). VII is reduced by Na and EtOH to p-cyclopentenylidimethylaniline, b₁₂ 156° (HCl salt, m. 175°; picrate, m. 134°; methiodide, m. 179°). In the reaction product of PhNH₂ and Me₂CO (Hosokawa, Ger. Pat. 399,141), in addn. to Me₂C(C₆H₄NH₂)₂ there may be observed a small fraction (about 1%) consisting of isopropenylaniline (VIII), b. 125-30° (pressure not given), which may be obtained in better yields by heating Me₂C(C₆H₄NH₂)₂ with a few drops of dil. HCl and H₂SO₄ in vacuo; the distillate consists of PhNH₂ and VIII in the ratio of about 2:1. VIII yields a HCl salt, m. 230-5°, a picrate, m. 180°; the Ac deriv., m. 110-1°; the phenylthiourea, m. 137°. VIII, freshly prepd., has d₄₂₀ 1.0320 and is a mobile liquid; on standing 40 hrs. there results a dimer or bisisopropenylaniline (IX), m. 173° (HCl salt, m. 228°; picrate, m. 172°; di-Ac deriv., m. 205°; phenylthiourea, m. 117°; these comds. could not be obtained from the corresponding derivs. of VIII). IX is unstd. towards KMnO₄, and the Ac deriv. is catalytically reduced; the dihydro deriv., m. 121°; sapon. gives the bisisopropenylaniline (X), b_{0.1} 205-10°, m. 50-2° (diphenylthiourea, m. 178°; picrate, m. 213°; HCl salt, m. 275°). X, through the diazo reaction, yields the phenol, Cl₃H₂CO₂, m. 106-7° (Bz deriv., m. 117°; Ac deriv., b_{1.0} 192°). Me₂CO and PhNHMe₂, heated 10 hrs. at 150° with HCl, give 50% of 2,2-dimethylaminodiphenylpropane, b_{1.5} 190°, m. 138° (HCl salt, m. 218°; Ac deriv. m. 139°; diphenylthiourea, m. 170°); distn. with a little acid gives equal parts of PhNHMe and *N*-methyl-p-isopropenylaniline, b₁₄ 123-5° (HCl salt, oily; Picrate, m. 147°); d. 0.9675, changes only to 1.0067 after heating 20 hrs. on the H₂O bath, indicating only slight polymerization. Me₂C(C₆H₄-Me)₂ give *N*-dimethylisopropenylaniline, b₁₅ 120-2°, m. 74° (HCl salt, m. 122°; picrate m. 96°); this also shows little tendency to polymerization. Me₂CO and *m*-MeC₆H₄NH₂ give about 9% of 3-methyl-4-isopropenylaniline (XI), b₁₃ 150-5° (HCl salt, m. 217°; picrate, m. 224°; Ac compd., oily), reduced to 3-methyl-4-isopropenylaniline, b₁₃ 141-5° (HCl salt, m. 211°) and 3% of 3-methyl-4,6-diisopropenylaniline, b₁₃ 225-30° (HCl salt, m. 218°; picrate, m. 205°). XI, warmed 16 hrs. at 100°, shows about 10% polymerization. 2,2-Diaminodiphenylbutane, b₃ 210° (20% yield); distn. with a little HCl or H₂SO₄ there results about 40% of p-isobutenylaniline, b₁₄ 140-5°, d₄₁₉ 0.9899 (HCl salt, m. 238°; picrate, m. 196°; phenylthiourea, m. 131°; Ac deriv., m. 121°); after standing 4 days and warming 24 hrs. at 100°, 75% is recovered unchanged while the rest is obtained as a dark red hard glass. 2,2-Dimethylaminodiphenylbutane, b₄ 240°, m. 98° (diphenylthiourea, m. 142°; di-Ac deriv., m. 121°); p-isobutenylaniline, b₁₄ 145-50°. 2,2-Tetramethyldiaminodiphenylbutane, b_{0.3} 210-2° (HCl salt, m. 125°; picrate, m. 80-90°; methiodide, m. 202°); p-isobutenylidimethylaniline, b₁₄ 138-42°, d₄₂₀ 0.9561 (picrate, m. 125°; dimethiodide, m. 175°); polymerization is scarcely noticeable. Me₂CO and PhNHMe₃ give 5% p-isobutenylidimethylaniline, b₁₂ 160-2° (methiodide, m. 175°), and 15% 2,2-tetramethyldiaminodiphenylhexane, b₄ 230-4° (dimethiodide, m.

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 196'). PhAc and PhMe2 give 20% of tetramethyldiaminotriphenylethane, m. 134° (dimethiodide, m. 188°), and 7-8% of p-phenylvinylidimethylaniline, b13 208-11°, d20 1.0409 (HCl salt, m. 144°; methiodide, m. 170°). Condensation of PhNH2 and PrCHO gives only 2-propyl-3-ethylquinoline; PrCHO and PhNH2 with 20% HCl and a little EtOH show about 30% condensation after 5 days at 100°, the principal product is 1,1-tetramethyldiaminodiphenylbutane, b0.3 225-7°, distd. with a little H2SO4 in vacuo there results 30% of a mixt. of PhNH2 and p-butenyldimethylaniline, the latter, b12 140-2°, d415 0.9395 (picrate, reddish yellow, m. 99-100°); it shows little tendency to polymerize, even on heating at 100° for 24 hrs., warming with PhNH2.HCl for 30 hrs. gives about 50% of 1,1-aminophenyl[dimethyldiaminophenyl]butane, b0.2 205-10°. In comparison with PrCHO, BzH and PhMe2 are almost completely condensed in 24 hrs.; p-Me2C6H4CHO is completely condensed in 24 hrs. and p-NO2C6H4CHO in about 18 hrs. In acid soln. 1 mol. of an aromatic aldehyde and 1 mol. of an aromatic aniline first condense to a very active product closely related but not identical with the basic hydrol. Condensation of 2 mols. PhOH and 1 mol. cyclohexanone, using 1/3 of the wt. of the latter of concd. HCl, at 36° gives, after 60 hrs. a 65% yield, consisting of 1,1-dihydroxydiphenylcyclohexane (XII) (di-Me ether, b16 260-3°, m. 82°; di-Ac deriv., m. 122°) (cf. Schmidlin and Lang, C. A. 5, 487), and a small amt. of o-cyclohexyldienecyclohexanone. Distn. of XII at the ordinary pressure gives PhOH, cyclohexenylphenol (XIII), m. 123° (Me ether, b14 155°, m. 35°; Ac deriv., m. 52°), and p-cyclohexenylphenol (XIV), m. 131° (Me ether, m. 58°; Ac deriv., b15 170°, m. 35°). XIII adds Br to the double bond before substitution occurs and this reaction may be used to det. the amt. of XIII present in the mixt. with XIV. Warming XIII with concd. HCl gives about 50% of XIV, while the other half is a resinous mass, similar to that obtained by the distn. of XII. Heating XII with Ni and H at 230-50° gives cyclohexanol, p-cyclohexylcyclohexanol (Schrauth and Gorig, C. A. 18, 388) (Ac deriv., b15 158-60°), and a partial reduction product of XII, C12H22O2, b13 260-70°. Cyclohexanone and m-MeC6H4OH, after 14 days, condense to the extent of 40%; cyclohexenylcresol, b12 175°; p-cyclohexyl-m-cresol, thick oil. o-Methylcyclohexanone and PhOH give methylcyclohexenylphenol, b12 173-5°, and the diphenylmethane compd., C12H22O2, b12 280°, m. 135-7°. Cyclopentanone and PhOH give 1,1-dihydroxydiphenylcyclopentane, b12 270°, m. 155-6° (Me ether, b12 240-5°, m. 115°; Ac deriv., m. 79°); heating with 3 parts concd. HCl 3 hrs. at 100° gives PhOH and p-cyclopentylphenol, b12 155° m. 63-5° (Me ether, b12 143°; Ac deriv., b12 150-2°); distn. of the diphenol at the ordinary pressure gives cyclopentylphenol, m. 148-50° (Me ether, m. 90°; Ac deriv., m. 72°). 4-Cyclopentylcyclohexanol, b12 135°, m. 43-50° (phenylurethane, m. 115-45°); this is a mixt. of 2 stereoisomers. Oxidation gives 4-cyclopentylcyclohexanone, b12 125°, nD18 1.4860, d418 0.9714 (semicarbazone, m. 195-7°). Me2CO and PhOH give after 60 hrs. practically quant. Me2C(C6H4OH)2, b13 250-2°, distn. at the ordinary pressure gives a small amt. of p-isopropylphenol, b12 112-5°, m. 61°; the action of 3 parts of concd. HCl for 20 hrs. at 100° gives a dimer, C18H20O2, b14 255-6°, m. 181°, which is stable towards HCl at 125°; the di-Me ether, m. 115°, is stable towards catalytic reduction or Na and EtOH; di-Ac deriv., m. 165°. Catalytic reduction (Ni) gives a mixt. of cyclohexanol, p-isopropylcyclohexanol, di-4-hydroxycyclohexyldimethylmethane, b14 230-4° (diketone, m.

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 [a]D23 -15.26° (CHCl3) (HCl salt, m. 185°); bisphenylthiourea, m. 105°). The corresponding dimethylaniline derivs. have [a]D23 46.65° and -20.94°. 3-Methylcyclohexylbenzene (XVII), b14 123-4°, [a]D20 -5.26° (cf. Kuranov, C. A. 1, 2093). p-Methylcyclohexylbromobenzene, in 60% yield from the diazo compd. and CuBr, b14 165-7°, d418 1.2100, [a]D18 -2.23°; the diazo compd. and CuCN give the nitrile, b14 166-8°, d413 1.0058, [a]D26 -1.62°. Reduction of the diazo compd. with SnCl2 gives 50% of p-3-methylcyclohexylphenylhydrazine, m. 84-5°, [a]D20 -4.99° (EtOH), relatively unstable (HCl salt, m. 210°; semicarbazide, m. 217-8°; thiosemicarbazide, m. 175°). XVIII and AcCl with AlCl3 give 85% of p-methylcyclohexylacetaphenone, b14 182-5°, d421 0.9986, [a]D21 -3° (semicarbazone, m. 211°). Methylcyclohexenyl-methylaniline, m. 33°, yields a yellow NO compd., m. 50°, reduced to the hydrazine, m. 34° [a]D15 39.12° (EtOH) (thiosemicarbazide, m. 181°); HCHO gives a hydrazone m. 121°, and BzH a hydrazone, m. 100°.

ACCESSION NUMBER: 1929:40433 CAPLUS
 DOCUMENT NUMBER: 23:40433
 ORIGINAL REFERENCE NO.: 23:4687g-1,4688a-1,4689a-1,4690a-g
 TITLE: Thermal and hydrolytic decomposition of basic and phenolic diphenylmethane derivatives and synthesis of optically active aromatic compounds
 AUTHOR(S): V. Braun, Julius; Anton, Ernst; Haensel, Werner; Werner, Georg
 SOURCE: Ann. (1929), 472, 1-89
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 158-60°; semicarbazone, m. 222°), and p-hydroxyphenyl 4-hydroxycyclohexyldimethylmethane (XV), b12 244-8° (di-Ac deriv., b16 234-7°, mono-Me ether, b1 170-5°). The last 2 compds. are probably mixts. of stereoisomers. Oxidation of XV with CrO3 gives the ketone, b15 205-10° (semicarbazone, m. 184°). Oxidation of XV with KMnO4 gives the substituted adipic acid, MeOC6H4Me2CCH2CH2C(=O)2H, m. 115° (45% yield). Me2CO and m-MeC6H4OH give the diphenol, b12 230-5°. MeEtCO and PhOH give a diphenol, b12 250-3°, which, on distn. at ordinary pressures, gives, as 1 product, p-isobutenylphenol, m. 86° (Ac deriv. b15 148°). Catalytic reduction with Ni at 200° gives the compd., C10H20O, an isomer of menthol, b20 128°, oxidized to the ketone, C10H18O, b12 104-6° (semicarbazone, m. 190°). EtCHO and PhOH give EtCH(C6H4OH)3 b15 250°, which, distd. at atm. pressure, gives p-propenylphenol, m. 89-91°, heating the latter 1 hr. at its b. p. gives a reddish oil, about half of which is p-PrC6H4OH. PrCHO gives 1,1-dihydroxydiphenylbutane (XVI), b12 270°, which on distn. gives p-butylphenol, b10 138-41° (Ac deriv., b15 138-41°). Catalytic reduction of XVI at 220° gives the compd. C16H24O2, b15 235-40° (di-Ac deriv., b14 230-4°), and 4-butylcyclohexanol, b15 120-2° d420 0.9106, nD15 1.4691, which yields 2 phenylurethanes, m. 124° and 42°, sepd. by crystn. from MeOH oxidation (CrO3) gives p-butylcyclohexanone, m. 101-2° (semicarbazone, m. 175°). PrCHO and m-MeC6H4OH give butenylcresol, b12 150° (Me ether, b12 130-3°; Ac deriv., b12 140°) and 1,1-dihydroxydi-m-tolylbutane, b12 250° (di-Ac deriv., b11 230-5°); heating 8 hrs. with 3 parts concd. HCl at 120-5° gives 3-methyl-4-butylphenol, b14 140-5°. Catalytic reduction of MeCH(C6H4OH)2 gives a mixt. of the compd. C14H20O2, b12 240° (mono-Me ether, b0.2 175-8°), and the compd. C14H22O2, m. 140-6° (a mixt. of isomers), oxidized to the ketone, C14H22O2, b15 225-30°, m. 55-6° (semicarbazone, m. 215-7°). Camphor (100 g.), 120 g. PhNH2 and 150 cc. 20% HCl, heated 14 days at 100°, give about 1 g. of the compd. C14H21N, b0.8 140°, [a]D14 (0.2090 g. in 2.2990 g. EtOH). Similarly 43 g. menthone, 88 g. PhNH2 and 80 cc. concd. HCl, heated 10 hrs. at 180°, give 2.5 g. of the compd. C18H27N, b12 195-205°, [a]D16 13° (10% in CHCl3). d-3-Methylcyclo-pentanone and PhNH2, heated several days at 100° in HCl soln., give about 4% of 3-methylphenyldimethylaniline, m. 64°, which shows scarcely any optical activity, and about the same yield of tetramethyldiaminodiphenyl-3-methylcyclopentane, m. 95°, [a]D21 22.50° (CHCl3). d-3-Methylcyclohexanone (XVII) and PhOH, condensed in the usual manner, give 56% of the diphenol, C12H22O2, b12 235-6°, m. 153-5°, [a]D20 -18.74° (EtOH); heating 4 hrs. at 100° with concd. HCl gives p-methylcyclohexylphenol, b14 170°, m. 60-75°, [a]D20 -6.94° (C6H6), identical with that obtained by fractional distn. of the product obtained by heating 3 hrs. at 100°. XVII and PhNH2 give the same products as the inactive compd., except that they are optically active; the diamine has [a]D23 -11.78° (CHCl3), the unsatd. amine [a]D20 54.21° (EtOH), 57.02° (CHCl3); a carefully prepd. sample of the diamine, b0.1 240-3°, has [a]D18 -16.21° (CHCl3), Methylcyclohexylaniline, m. 146°, [a]D17 -4.78° (EtOH); methylcyclo-hexylphenol, m. 60°, [a]D20 -6.9° (C6H6). Methylcyclohexenylmethylaniline, b15 192-5°, m. 33°, [a]D18 47.63° (CHCl3) (HCl salt, m. 180°); 1,1-dimethylaminophenyl-3-methyl-cyclohexane, b1.5 260-5°,

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 AB If care is taken in the design of the distillation apparatus to see that all vapors volatilized pass over into the condenser and collecting flask, the following equation represents the change in composition of the liquid on distillation: (log y1 - log y2)/(log x1 - log x2) = k, where x and y refer, resp., to the quantities of water and of volatile organic compound and subscripts 1 and 2 refer, resp., to the quantities at the beginning and end of the distillation. By this equation, the purity of a solution of organic compound such as a fatty acid can be proved by the constancy of k in successive distillation fractions. The influence of initial concentration and that of distillation on the value of k for dilute solns. of formic, acetic, propionic and butyric acids was studied. Concentration affects k only to a slight extent but the time of distillation influences k significantly so that it must be kept within close limits in quant. work. The rate of distillation adopted was 100 cc. of an original volume of 200 cc. in 60 min. A mixture of 2 volatile compds. e. g. 2 fatty acids, can be analyzed by determining the total acidity of the initial solution and of the distillate when half of the solution has passed over, provided that k for each of the acids is known. A mixture of 3 acids can be analyzed by determining the total acidity of initial solution and distillates when 1/4 and 1/2 of the sample has passed over. When more than 3 acids are present the exptl. errors become too large. If a compound has a value for k greater than 5 the exptl. errors are too large. Values for k are given for the following acids: formic 0.398, acetic 0.657, propionic 1.270, butyric 2.02, diethylacetic 4.57, chloroacetic 0.047, phenylacetic 0.070, pyruvic 0.074, α-crotonic 0.760, benzoic 0.270, salicylic 0.688, o-toluic 0.508, m-toluic 0.420, p-toluic 0.378, anisic 0.050, cinnamic 0.102, o-aminobenzoic 0.019; m- and p-aminobenzoic and the 3 nitrobenzoic acids do not distil. Approx. values of k for amines are: ammonia 13, methylamine 11, ethylamine 20, propylamine 30, butylamine 40, diethylamine 43, ethylenediamine 0.02, aniline 5.51, methylaniline 16, benzylamine 3.25, α-naphthylamine 1.05, β-naphthylamine very large. For phenols k is: phenol 1.94, p-chlorophenol 1.30, p-nitrophenol 0.005, m-nitrophenol 1.01, thymol 12; for aldehydes: formic 2.6, acetic 40, benzoic 18, anisic 3.1; for alcs.: methyl 8.9, ethyl 12.9. The volatility of a compound with steam increases as the hydration in solution decreases. Neutral salts influence the volatility by altering the hydration, usually decreasing hydration and increasing k. Anions have a greater influence than cations. A given salt has a greater influence on less soluble than on more readily soluble volatile compds. There is a striking parallel between the action of salts on the volatility and on the adsorption of compds. from solution by charcoal.

ACCESSION NUMBER: 1928:36643 CAPLUS
 DOCUMENT NUMBER: 22:36643
 ORIGINAL REFERENCE NO.: 22:4351f-1,4352a-b
 TITLE: The distillation of water-soluble organic substances with steam
 AUTHOR(S): Vitanen, Artturi I.; Pulkki, L.
 SOURCE: Ann. acad. sci. Fennicae (1927), 29A, 28 pp.
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L14 ANSWER 35 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diagram(s), see printed CA issue.
 AB (Cf. Ibid., 24, 614)-2-Methyl-4-methylaminoheptanol (6) was prepared from α -isomethylheptenone and methylamine and subsequent reduction, and its reactions studied. Experimental. α -isomethylheptenone, (Ber., 33, 561), $(CH_3)2CH.CH_2.CH:CH.COCH_2$, and methylamine at -10 to -20° , acidified and then reduced with sodium amalgam on distillation yielded 2-methyl-4-methylaminoheptanol (6), $(CH_3)2CH.CH_2CH(NHCH_3).CH_2CH(OH).CH_3$, b13 $106-107^\circ$. On methylation and with gold chloride, the chloraurate $(C_9H_{20}NO.CH_2.CH_3Cl)$ AuCl₂, m. 129° , was found, and with nitrous acid, the nitrosamine was prepared. The aminoalcohol and formaldehyde yielded a tetrahydromethoxazine derivative, $(CH_3)2CH.CH_2CH(CH_2CH(CH_3)N(CH_3).CH_2O$, b13 $83.5-84^\circ$. Chloraurate, m. $130-134^\circ$, chloroplatinate, which added methyl iodide at the ordinary temperature, and formed double salts of the methylated product with gold and platinum chlorides. With chlorocarbonic ester the aminoalcohol yielded the lactone of the carbonic acid, $(CH_3)2CH.CH_2.CH(CH_2CH(CH_3)N(CH_3)C.H_2O$, b11 170.5° . With ethylene oxide a basic glycol, $(CH_3)2CH.CH_2CH_2CH(CH_2CH(OH).CH_3).N(CH_3).CH_2.CH_2OH$, b13 $161-162^\circ$, was formed. The aminoalcohol and HBr yielded the hydrobromide of 6-brom-4-methylamino-2-methylheptane, which with alkali produced N- α -dimethyl- γ -isobutyltrimethylselenimine, $(CH_2)2CH.CH_3.CH(CH_2N(CH_3)CH_3).CH_3$, b. $152-154^\circ$, picrate, m. $93-94^\circ$. Methyl iodide, (the methyl chloride, its chloraurate, m. $63-64^\circ$, and chloroplatinate, m. $170-171^\circ$ with decomposition, were also prepared), treated with alkali yielded a tertiary base, C₁₀H₂₁N, b. $168-71^\circ$, chloroplatinate, m. $135-38^\circ$, picrate, b. $84-85^\circ$, which was unsaturated and of which the methyl iodide (chloraurate of the methyl derivative, m. $75-80^\circ$), and its chloroplatinate, m. $155-156^\circ$ with decomposition, with silver oxide formed the ammonium compound, which on dry distillation yielded H₂O, (CH₃)₃N, and an unsaturated hydrocarbon, C₈H₁₄, taking up two atoms of bromine at 0° . The structural formulas of the compounds, C₁₄H₂₁N and C₂H₂₄ are not established as yet.

ACCESSION NUMBER: 1907:10756 CAPLUS
 DOCUMENT NUMBER: 1:10756
 ORIGINAL REFERENCE NO.: 1:2564d-1,2565a
 TITLE: The Preparation of Aminoalcohols from Unsaturated Methylketones. II Communication
 AUTHOR(S): Kohn, Moritz; Glasconi, Jakob
 CORPORATE SOURCE: Univ. Vienna
 SOURCE: Monatshefte fuer Chemie (1907), 28, 461-78
 CODEN: MOCHB7; ISSN: 0026-9247
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L14 ANSWER 36 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diagram(s), see printed CA issue.
 AB Some years ago the author found that the methylene bases, RNCH₂NHR, unlike the corresponding ethylene derivatives, do not yield closed chain compounds with diphenyl oxalate (Ber., 35, 3440) but hydroxybenzylamine derivatives, HOC₆H₄CH₂NHR, and oxalylarylamides, RNHCOONHR. In certain cases, however, especially with p-tolyl derivatives, the secondary base is converted into an equimolecular mixture of primary, H₂NR, and tertiary base, RN₂R, which latter, with phenols, yield the above hydroxybenzylamine compounds. Phenol and the secondary methylene bases give phenol salts of primary bases, PhONHR and a mixture of the components. The methylene usually enters the phenol ring in the ortho position, but in the case of orthomethoxybenzene and paraethoxybenzene the methylene enters at the para position. In the above cases R = C₆H₅, o-C₆H₄CH₃, o-C₆H₄CH₃, p-C₆H₄CH₃, p-C₆H₄OC₂H₅. N,N'-diphenylmethylenediamine, PhNH.CH₂NHPh. This base gives, with phenol, a hydroxybenzylamine, microscopic prisms, m. 156° and also the ortho isomeride, m. 113° , which is likewise formed from phenol and "anhydroformaldehyde aniline." Resorcinol yields a 1,3-dihydroxybenzylamine, (HO)2C₆H₃CH₂NHPh, crystalline powder consisting of small rods. It could not be benzoylated. Diphenyl oxalate gives oxanilide and o-hydroxybenzylamine. Sodium phenolate resolves the base into aniline. The base does not react with acetone, alcoholic potassium hydroxide, ethyl acetate, or benzaldehyde. Ethyl oxalate, ethyl malonate and ethyl succinate, on the other hand, yield the anilides of the respective acids and a mixture of tertiary "anhydro" bases. N,N'-Diorthotolylmethylenediamine. Prepared from o-toluidine hydrochloride and formaldehyde by an improved method. Yield, 50%. Aniline, under the same conditions, gives only mixtures of "anhydroformaniline." With phenol the above base gives, in very small quantity, what is probably o-hydroxybenzyl-o-toluidine; transparent plates, m. $40-50^\circ$. Diphenyl oxalate yields oxal-o-anilide, m. 210° . N,N'-Diparatolylmethylenediamine. With phenol o-hydroxybenzyl-p-toluidine is formed. Resorcinol yields m-dihydroxybenzyl-p-toluidine, (HO)2C₆H₃CH₂NHCH₃OMe, microscopic rods or plates, m. 165° . Diphenyl oxalate gives oxal-p-toluide and "anhydroformtoluidine," a mixture of tertiary bases, m. $127-128^\circ$ and $212-223^\circ$, respectively. (vide Ber., 31, 3253). N,N'-Diorthoanisylmethylenediamine. The base b20 160° ; distillation with phenol does not cause a reaction. At $180-200^\circ$ a hydroxybenzyl-o-anisidine, is formed, microscopic rods, m. 125° . It is probably the p-compound. The ortho isomer was also obtained by boiling the reacting substances in benzene. With diphenyl oxalate, oxalo-o-anisidine is formed, hexagonal plates, m. 246° . It was prepared for comparison from diphenyl oxalate and o-anisidine. p-Nitrophenol, pyrocatechol, resorcinol and hydroquinol could not be induced to act on this diamine and all attempts to prepare an "anhydro base" were fruitless. N,N'-Diparaanisylmethylenediamine. Phenol and p-anisidine combine, in ligroin solution, forming the phenolate, C₁₈H₁₆O₂N₂, colorless prisms, m. 60° . With the methylene base phenol yields o-hydroxybenzylanisidine. Diphenyl oxalate forms oxanisidine and resorcinol gives 1,3-dihydroxy-p-anisidine, (HO)2C₆H₃CH₂NHCH₃OMe, colorless thin plates, m. 149° ; at 140° it becomes red. N,N'-Diparaphenethylmethylenediamine, b12 174° ; boiling in air resolves it into its constituents. No formation of tertiary base could be observed. Phenol and phenetidine yield the phenolate, long, lustrous needles, m. 52° . Phenol and the methylene base give a mixture of products, but in benzene solution a hydroxybenzyl-p-phenetidine is formed; small prisms, m. 106° . It becomes yellow in air and is probably

L14 ANSWER 36 OF 36 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 the para compound. Diphenyl oxalate yields only oxalphenetide. With resorcinol 1,3-dihydroxybenzylphenetidine, (HO)2C₆H₃CH₂NHC₄H₉OEt, is formed; irregular, thin plates, m. 156° . In addition to the above methylene bases the action of a number of others on diphenyl oxalate has been studied. Methylaniline gives a mixture of dimethyloxanilide, PhNHMeCOONMePh, colorless crystals, m. 86° and phenyl methyloxanilate, PhNHMeCOO2Ph, oil, b10 about 270° . The "methyloxanilide" of Norton and Livermore (Ber., 20, 2273), b. $249-251^\circ$, cannot be a derivative of oxalic acid, but may, perhaps, be methylformanilide. Phenylhydrazine and diphenyl oxalate give oxalylidiphenylhydrazide, which has been previously prepared by E. Fischer from diethyl oxalate. Phenyl phenyloxanilate, PhZNCOCOCOPh, from diphenyl oxalate and diphenylamine; prisms, m. $127-128^\circ$. Phenyl benzyloxanilate, PhCH₂NHPhCOCOCOPh, from diphenyl oxalate and benzyaniline; colorless prisms, m. $93-94^\circ$. Carbazole and diphenyl oxalate could not be induced to interact.

ACCESSION NUMBER: 1907:1663 CAPLUS
 DOCUMENT NUMBER: 1:1663
 ORIGINAL REFERENCE NO.: 1:4169-i,417a-i
 TITLE: Resolution of N, N'-Diarylmethylenediamines
 AUTHOR(S): Bischoff, C. A.; Frohlich, E.
 CORPORATE SOURCE: Synthetic Lab., Polytechnicum, Riga
 SOURCE: Ber. (1907), 39, 3964-81
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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=> s secondary
      410236 SECONDARY
      1798 SECONDARIES
L15   411299 SECONDARY
      (SECONDARY OR SECONDARIES)

=> d his

      (FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

      FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005
L1    1 S FORMALDEHYDE/CN

      FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005
L2    61794 S 50-00-0/RN
L3    166261 S N-METHYL?
L4    1415128 S ?AMINE
L5    889 S L2 AND L3 AND L4
L6    362618 S DISTILL?
L7    47 S L5 AND L6
L8    135208 S FORMALDEHYDE
L9    53548 S L8 AND L2
L10   143454 S L8 OR L2
L11   3718 S L10 AND L3
L12   2315 S L11 AND L4
L13   2268 S L12 NOT L7
L14   36 S L13 AND L6
L15   411299 S SECONDARY

=> s l15 and l9
L16   1271 L15 AND L9

=> s l16 and l6
L17   72 L16 AND L6

=> s l17 not l7
L18   65 L17 NOT L7

=> s l18 not l14
L19   65 L18 NOT L14

=> d l19 1-65 abs ibib

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L19 ANSWER 1 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN

AB A process for the preparation of 1-substituted-4-substituted-aminomethyl-1,4-pentadien-3-ones (I; e.g., 1-p-anisyl-4-piperidinomethyl-1,4-pentadien-3-one), useful as anti-H.I.V. and spermicidal agents, comprises: (i) heating a 1-substituted-1-buten-3-one (e.g., cis- and trans-p-anisylidenacetone) with a secondary amine (e.g., piperidine) or its salts and a formaldehyde solution in the presence of a lower C2-3 aliphatic alc. (e.g., ethanol); (ii) removing the aliphatic alc. by distillation under reduced pressure; (iii) neutralizing the obtained residue with an aqueous alkali bicarbonate (e.g., sodium bicarbonate) solution; (iv) extracting the reaction mixture with an organic solvent; (v) evaporating off the solvent; (vi) chromatographing the residue; (vii) heating the obtained 1,5-disubstituted-1-penten-3-one (e.g., 1-p-anisyl-4-piperidinomethyl-1-buten-3-one) with paraformaldehyde in the presence of a C2-4 aliphatic acid (e.g., acetic acid); (viii) removing the aliphatic acid by vacuum distillation; (ix) neutralizing the residue with an aqueous alkali bicarbonate solution; (x) extracting the reaction mixture with an organic solvent; (xi) evaporating off the solvent; and (xii) chromatographing the residue to obtain I.

ACCESSION NUMBER: 2004:1044567 CAPLUS
DOCUMENT NUMBER: 141:424110
TITLE: Process for the preparation of 1-substituted-4-substituted-aminomethyl-1,4-pentadien-3-ones useful as anti-H.I.V. and spermicidal agents
INVENTOR(S): Khanna, Nandoo Mal; Dwivedi, Anil Kumar; Pal, Raghvendra; Singh, Satyawan; Setty, Bachu Srinivasulur; Kambaj, Vee Prakash
PATENT ASSIGNER(S): Council of Scientific and Industrial Research, India
SOURCE: Indian, 14 pp.
CODEN: INXXAP
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
IN 186313	A	20010804	IN 1996-DE2629	19961129
PRIORITY APPL. INFO.:			IN 1996-DE2629	19961129
OTHER SOURCE(S):			CASREACT 141:424110	

L19 ANSWER 3 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN

AB Removal of trimethylolpropane formate from trimethylolpropane (I), as produced by the hydrogenation of 2,2-dimethylolbutanal, is achieved by drying the raw solution of hydrogenation product and addition of ammonia or primary and/or secondary amines in anhydrous form. Thus, PrCHO was condensed with aqueous HCHO in the presence of Et3N at 40°, and the lower-boiling reactants and byproducts were removed in a thin-film evaporator and recycled. The heavier fraction was passed through a second-stage reaction with addnl. Et3N in a tubular reactor at 40° and the product was hydrogenated over a catalyst containing Cu 20, CuO 24, and TiO2 46% and H2O was distilled to give a crude I fraction containing 82% I and 7% I monoformate. The crude I was mixed with Me2NH and heated at 120° for 34 min to give complete conversion of the I monoformate to addnl. I, as well as DMF.

ACCESSION NUMBER: 2001:489340 CAPLUS
DOCUMENT NUMBER: 135:93381
TITLE: Method for the conversion of trimethylolalkane formate arising during manufacture of trimethylolalkane
INVENTOR(S): Dornbach, Matthias; Kratz, Detlef; Stammer, Achim; Schulz, Gerhard
PATENT ASSIGNER(S): BASF A.-G., Germany
SOURCE: PCT Int. Appl., 24 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001047849	A1	20010705	WO 2000-EP13327	20001228
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
DE 19963444	A1	20010712	DE 1999-19963444	19991228
PRIORITY APPL. INFO.:			DE 1999-19963444	A 19991228
REFERENCE COUNT: 4			THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT	

L19 ANSWER 2 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN

AB A method of separation of lower aliphatic acids from aqueous solns. containing formic acid comprises reacting a mixture of lower aliphatic acids with amines in the presence of formaldehyde and subjecting the resulting salts to thermal decomposition with simultaneous distillation of the acids. The invention makes use of removing formic acid from the aqueous solns. of lower carboxylic acids by reductive alkylation of primary and secondary amines in the presence of formaldehyde. Formic acid is removed from the initial mixture by adding (i) 0.5-0.53 mol of primary amines or 1.0-1.03 mol of secondary amines of the general formula R1R2NH, where R1 is an aliphatic hydrocarbon radical with 6-25 carbon atoms, and R2 is hydrogen or an aliphatic hydrocarbon radical with 1-25 carbon atoms, and (ii) 1.0-1.03 mol of formaldehyde per 1 mol of formic acid, the process being carried out at 50-80°. Tertiary amines formed during the process form salts with the carboxylic acids present in the solution, addnl. amount of pure tertiary amines being added to provide complete conversion to salts.

ACCESSION NUMBER: 2003:444608 CAPLUS
DOCUMENT NUMBER: 140:130112
TITLE: Method of separation of lower aliphatic acids from aqueous solutions containing formic acid
INVENTOR(S): Fakhretudinov, F. S.; Romanov, G. V.; Mizipov, I. R.
PATENT ASSIGNER(S): Institut Organicheskoi i Fizicheskoi Khimii im. A. E. Arbuzova Kazanskogo Nauchnogo Tsentra RAN, Russia
SOURCE: Russ., No pp. given
CODEN: RUXOEX
DOCUMENT TYPE: Patent
LANGUAGE: Russian
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
RU 2197471	C1	20030127	RU 2001-117948	20010628
PRIORITY APPL. INFO.:			RU 2001-117948	20010628
OTHER SOURCE(S):			MARPAT 140:130112	

L19 ANSWER 4 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN

AB Trimethylolalkanes (e.g., trimethylolpropane) are prepared in high yield and selectivity by the reaction of alkanals (e.g., n-butyraldehyde) and formaldehyde in the presence of a tertiary amine (e.g., triethylamine) and water, followed by a step for the distillation of the tertiary amine and water such that the formaldehyde-alkanal reaction mixture is heated so that formate byproduct salts (e.g., triethylammonium formate) of the tertiary amine are thermally dissociated, and the formate ester byproducts of the trimethylolalkane in the residue are reacted with water and a primary or secondary amine to produce the corresponding formaldehydes which are easily removed from the trimethylolalkane product.

ACCESSION NUMBER: 1999:286252 CAPLUS
DOCUMENT NUMBER: 130:282806
TITLE: Method for the high-yield preparation of trimethylolalkanes from the reaction of alkanals and formaldehyde
INVENTOR(S): Doi, Kenji; Jinno, Takuhiko; Moriyama, Ayao; Uji, Shingo
PATENT ASSIGNER(S): Koel Chemical Co., Ltd., Japan
SOURCE: Ger. Offen., 8 pp.
CODEN: GWXXEX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 19848568	A1	19990429	DE 1998-19848568	19981021
CN 1219527	A	19990616	CN 1998-120446	19981020
CN 116262	B	20030730		
US 6034284	A	20000307	US 1998-175431	19981020
SG 79241	A1	20010320	SG 1998-4230	19981020
IT 1305123	B1	20010410	IT 1998-T0888	19981020
IT 98T0088	A1	19990422		
TW 555741	B	20031001	TW 1998-87117387	19981021
JP 11199531	A2	19990727	JP 1998-301428	19981022
PRIORITY APPL. INFO.:			JP 1997-309232	A 19971022
			JP 1997-327059	A 19971111

L19 ANSWER 5 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB An increasing number of publicly owned treatment works (POTWs) are reporting difficulties in complying with cyanide permit levels set by their states and some are facing legal action by public challengers in the light of being unable to control these apparent permit violations. Part of this problem is the impossible burden placed on utilities and their contract anal. labs. to determine cyanide levels often at or below the practical quantitation limit of 10 µg/L set by the US EPA for the currently approved anal. methodol. The methodol. is cumbersome, unreliable, and in many cases fails to effectively recover measured addns. of cyanide in the matrix being analyzed. There have been instances of apparent levels of cyanide in the chlorinated effluents of plants that had no measurable level in their secondary effluents. An alternative technique to the existing EPA approved methodologies should take advantage of modern separation techniques using automation and providing for rapid sample throughput with the minimal of sample handling. We evaluated an alternative procedure for the anal. of total cyanide in wastewaters which utilizes segmented flow injection for sample transport and reaction, on line acidic UV digestion for conversion of complexed cyanide to HCN, and amperometric detection achieved within 4 min of sample injection. Grab samples were collected from different points in a variety of wastewater treatment plants and split for simultaneous anal. of total cyanide at 3 different labs. Samples were analyzed by both the standard EPA method and the FIA method developed here. The application of this latter methodol. to the anal. of wastewaters compares favorably with the traditional methodol. when the latter is used under strict quality control protocols. However, when high cyanide values were obtained using the distn./colorimetric approach (EPA method), they were also obtained with the flow injection method. This paper reports the procedures to minimize cyanide formation during wastewater treatment and the subsequent anal. Guidance is provided for appropriate sample handling, screening, and processing in order to assure valid anal. results.

ACCESSION NUMBER: 1999:256487 CAPLUS
 DOCUMENT NUMBER: 130:342628
 TITLE: Application of flow injection for the analysis of total cyanide in wastewater treatment plant effluents
 AUTHOR(S): Weinberg, H. S.; Cook, S. J.; Singer, P. C.
 CORPORATE SOURCE: Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, NC. 27599-7400, USA
 SOURCE: Proceedings - Water Environment Federation Annual Conference & Exposition, 71st, Orlando, Fla., Oct. 3-7, 1998 (1998), Volume 1, 237-246. Water Environment Federation: Alexandria, Va.
 CODEN: 67NFAZ
 DOCUMENT TYPE: Conference
 LANGUAGE: English
 REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L19 ANSWER 7 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB 1,3-Dioxolane (I) is prepared by treatment of ethylene glycol (II) with HCHO or substances generating HCHO in the presence of acid catalysts, distillation of the reaction mixts., concentration of the distillates with or after addition of alkali substances, treatment of the concentrated solns. with Cl-4 alkyl-substituted benzene to extract I, and distillation of the exts. to remove low-b.p. impurities and the extraction solvents. II was treated with aqueous HCHO and H2SO4 at 115°, distilled, further distilled with feeding aqueous NaOH, extracted with MePh, and distd to give high-purity I.

ACCESSION NUMBER: 1998:498639 CAPLUS
 DOCUMENT NUMBER: 129:122656
 TITLE: Preparation and purification of 1,3-dioxolane
 INVENTOR(S): Kuriyama, Ikuhisa; Kondo, Takao; Nakatani, Daigo; Yamada, Kenji
 PATENT ASSIGNEE(S): Mitsubishi Gas Chemical Co., Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
 CODEN: JKOXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 10204060	A2	19980804	JP 1997-12741	19970127
PRIORITY APPLN. INFO.:			JP 1997-12741	19970127
OTHER SOURCE(S):			MARPAT 129:122656	

L19 ANSWER 6 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Title process is carried out by previously treating methacrylic acid-containing materials (prepared by vapor-phase contact oxidation of C4 compds.) with primary and/or secondary amino group-containing compds., treating with strongly acidic cation exchange resins, then mixing with formaldehyde-containing materials, flowing through a strongly acidic cation exchange resin-charged fixed bed, and distilling the treated product. Thus, 100 g crude methacrylic acid (prepared by vapor-phase contact oxidation of isobutylene; color number APHA63; purity 99.2%) was treated with 0.05 g ethylenediamine in the presence of 0.05 g phenothiazine, simple-distilled, treated with 2.5 g Amberlyst 15E (strongly acidic cation exchange resin) in the presence of 0.02 g hydroquinone, freed of Amberlyst 15E, mixed with 100 ppm formaldehyde, flowed through an Amberlyst 15E-charged fixed bed, and simple-distilled to give purified methacrylic acid (recovery 94%; color number APHA3).

ACCESSION NUMBER: 1999:142347 CAPLUS
 DOCUMENT NUMBER: 130:197101
 TITLE: Purification process of methacrylic acid for purified product with less discoloration and good performance of polymerization
 INVENTOR(S): Yoshida, Koichi; Kobayashi, Yoshiaki; Okita, Motomu
 PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
 CODEN: JKOXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 11060536	A2	19990302	JP 1997-216119	19970811
PRIORITY APPLN. INFO.:			JP 1997-216119	19970811

L19 ANSWER 8 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Treating RCH2CHO (I; R = H, hydrocarbyl) with formaldehyde in an aqueous medium in the presence of a C6-8 secondary amine and a C6-12 aliphatic carboxylic acid gives title compds. RC:(CH2)CHO and the amine and the acid are recovered and recycled. Thus, propionaldehyde, 37% formalin, di-n-butylamine (II), and caprylic acid (III) were fed continuously into an autoclave under N at 130° and 40 kg/cm2, the reaction mixture was collected under ice cooling and distilled to recover methacrolein (in 94.8% yield) together with H2O from the top, the bottom containing II and III was mixed with NaOH and distilled to recover 72% of II, and the residue was mixed with 20% H2SO4 and hexane to recover 98% of III from the organic layer.

ACCESSION NUMBER: 1995:275379 CAPLUS
 DOCUMENT NUMBER: 122:132585
 TITLE: Manufacture of α-methylenealdehydes
 INVENTOR(S): Nagareda, Katsushi; Yoshimura, Noriaki
 PATENT ASSIGNEE(S): Kuraray Co., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
 CODEN: JKOXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 06263683	A2	19940920	JP 1993-52485	19930312
JP 3324820	B2	20020917	JP 1993-52485	19930312
PRIORITY APPLN. INFO.:			JP 1993-52485	19930312
OTHER SOURCE(S):			MARPAT 122:132585	

L19 ANSWER 9 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB The title compound [(MeO)2P(O)CH2NH]2C:NCN is prepared by phosphonomethylation of cyanoguanidine with (MeO)2POH and HCHO in the presence of a catalyst, such that in order to avoid secondary reactions the HCHO and cyanoguanidine are introduced to the di-Me phosphite as a PhMe solution in a molar ratio of 2:1:2, with holding of the suspension at 55-60° and addition of MeONa in MeOH (447 g/L) to cause an exotherm; the water formed during the reaction is removed as an azeotrope with MeOH by distn., raising the temperature of the reaction mass to 70-80° for 3-5 h. In an example, 170 g of the desired product is obtained from 0.5 mol cyanoguanidine.

ACCESSION NUMBER: 1994:680882 CAPLUS
 DOCUMENT NUMBER: 121:280882
 TITLE: Preparation of tetramethyl cyanoguanidinobis(methanadiphosphonate)
 INVENTOR(S): Petrov, Pavel; Braitiu, Melania
 PATENT ASSIGNEE(S): Intreprinderea Textila, Timisoara, Rom.
 SOURCE: Rom., 3 pp.
 CODEN: RUJGAA3
 DOCUMENT TYPE: Patent
 LANGUAGE: Romanian
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
RO 103190	B1	19920613	RO 1988-136908	19881224
PRIORITY APPLN. INFO.:			RO 1988-136908	19881224

L19 ANSWER 11 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB In preparation of the title compds. by treating corresponding 1 mol part R1CH2CHO (I; R1 = H, Cl-10 alkyl) with 1-1.5 mol part HCHO in the presence of catalysts containing organic carboxylic acids (C) and secondary amines (A) at equivalent ratios of C/I 1-5 and C/A 0.5-2, the reaction is conducted at 30-120° in completely stirred tank reactors until 50-90% I-conversion at the 1st step, subsequently at 30-120° in piston-flow type reactors to complete the reaction at the 2nd step, followed by distillation of reaction solns. at 80-150° in decomposition column to give the title compds. A completely stirred tank reactor was fed with aqueous HCHO 1, EtCHO 1, EtCO2H 2, Bu2NH 2 mol, and H2O at 90° for 30 min (85% I conversion), the reaction solns. were fed into a piston-flow type reactor at 90° for 20 min to complete the reaction, the obtained reaction solns. were distilled at 105° for 20-25 min in a decomposition column to give 69.3 g methacrolein.

ACCESSION NUMBER: 1992:591335 CAPLUS
 DOCUMENT NUMBER: 117:191335
 TITLE: Preparation of α -alkylacroleins
 INVENTOR(S): Matsuoka, Kazuyuki
 PATENT ASSIGNEE(S): Daicel Chemical Industries, Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 5 pp.
 CODEN: JKKXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 04173757	A2	19920622	JP 1990-300135	19901106
PRIORITY APPLN. INFO.:			JP 1990-300135	19901106
OTHER SOURCE(S): MARPAT 117:191335				

L19 ANSWER 10 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB α -Alkylacroleins CH2:CR1CHO (I; R1 = H, Cl-10 alkyl, allyl) are prepared by reacting R1CH2CHO with HCHO (II) in the presence of a primary or secondary amine (0.01-10.0 equiv/1 mol I) catalyst having buffer capability. The reaction is carried out at 20-150°, 0.1-50 atom, and pH 2.5-12.0. New catalysts found such as amine salts of boric acid, phosphoric acid, carboxylic acids, and carbonic acid (derivs.) are free from environmental problems and the process gives 1 of excellent stability in high yields and selectivity under relatively mild conditions in a short reaction time. Thus, a solution of an oxalic acid amine salt was formed from 1260 parts (10 mol) oxalic acid dihydrate, 1050 parts (10 mol) (HOCH2CH2)2NH, and 2000 parts H2O, thereto 857 parts (10 mol) 35% aqueous HCHO and 580 parts (10 mol) MeCH2CHO were added, and the mixture was kept at 60° for 5 min to give after separation and distillation 92.6% methacrolein. No polymerization was observed after keeping the product at 20° for 2 days.

ACCESSION NUMBER: 1993:212487 CAPLUS
 DOCUMENT NUMBER: 118:212487
 TITLE: Preparation of α -alkylacroleins by Mannich reaction
 INVENTOR(S): Nakano, Tatsuya; Komoritani, Masahiro
 PATENT ASSIGNEE(S): Daicel Chemical Industries, Ltd., Japan
 SOURCE: Jpn. Kokai Tokkyo Koho, 15 pp.
 CODEN: JKKXAF
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 04338355	A2	19921125	JP 1991-111588	19910516
JP 2945165	B2	19990906	JP 1991-111588	19910516
PRIORITY APPLN. INFO.:			JP 1991-111588	19910516
OTHER SOURCE(S): CASREACT 118:212487; MARPAT 118:212487				

L19 ANSWER 12 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB 2-Methylalkanal are obtained from mixts. of isomeric aldehydes (from hydroformylation of isomeric olefins) by distillation in the presence of HCHO and an aldol reaction catalyst. Thus, an aldehyde mixture (from Rh-catalyzed hydroformylation of crude 2-methyl-1-butene) containing 2,3-dimethylbutanal (I) 69.57, 3-methylpentanal (II) 21.13, and 4-methylpentanal (III) 7.46 weight% was treated with formalin, Bu2NH, and PrCO2H and fractionally distilled at 0.1 MPa. Of 5 fractions, the 2nd containing 79.9% of the original I had a composition of I 97.14, II 0.01, and III 1.24% by gas chromatog.

ACCESSION NUMBER: 1990:138600 CAPLUS
 DOCUMENT NUMBER: 112:138600
 TITLE: Preparation of 2-methylalkanal from mixtures of isomeric aldehydes by treatment with formaldehyde
 INVENTOR(S): Weber, Juergen; Lappe, Peter; Springer, Helmut
 PATENT ASSIGNEE(S): Hoechst A.-G., Fed. Rep. Ger.
 SOURCE: Eur. Pat. Appl., 7 pp.
 CODEN: EPXKDW
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 335221	A2	19891004	EP 1989-104991	19890321
EP 335221	A3	19900207		
EP 335221	B1	19931229		
R: CH, DE, FR, GB, IT, LI, NL, SE				
DE 3811039	A1	19891019	DE 1988-3811039	19880331
CA 1313680	A1	19930216	CA 1989-594386	19890321
JP 01287050	A2	19891117	JP 1989-76885	19890330
JP 06078261	B4	19941005		
US 5064508	A	19911112	US 1990-574609	19900828
PRIORITY APPLN. INFO.:			DE 1988-3811039	A 19880331
			US 1989-325660	B1 19890320
OTHER SOURCE(S): CASREACT 112:138600; MARPAT 112:138600				

L19 ANSWER 13 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB In the manufacture of tertiary amines by the reaction of primary or secondary amines with HCHO in the presence of a hydrogenation catalyst, the reaction product is distilled after the addition of a primary or secondary amine. This method yields a high purity product with reduced discoloration and improved storage stability. Thus, pentamethyldiethylenetriamine, obtained by the reaction of diethylenetriamine with 37% HCHO, in the presence of Pd(S4)/C under H₂, was mixed with triethylenepentamine and distilled to give a product with ≥99.0% purity which had color APHA 10 as prepared, and 100 after 3 mo storage at 60°, vs. APHA 50 as prepared and 300 after 10 days for a control distilled without the addition of an amine.

ACCESSION NUMBER: 1987:140108 CAPLUS
DOCUMENT NUMBER: 106:140108
TITLE: Tertiary amines
INVENTOR(S): Torimoto, Yoshiaki; Yokota, Yukinaga; Hashiba, Ikizo; Matsuura, Kazuo
PATENT ASSIGNEE(S): Kao Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKOXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 61236751	A2	19861022	JP 1985-77770	19850412
PRIORITY APPLN. INFO.:			JP 1985-77770	19850412

L19 ANSWER 14 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Methacrylic acid (I) [79-41-4] prepared by gas-phase oxidation of C₄ compds.
was purified by treating with HCHO [50-00-0], H₂SO₄ or a sulfonic acid derivative, and optionally a primary secondary amine. Thus, 1 kg 98.5% I (by oxidation of isobutane, APHA color 77) was treated with phenothiazine 0.5, 98% H₂SO₄ 0.5, and formalin 1 g at 60° for 10 min and distilled at 30 torr to give I (yield 99.5%, APHA color 10) having polymerization induction period (in the presence of 2,2'-azobis(2-amidinopropane).2HCl, 65°) 3 min, compared with 22 min before the purification

ACCESSION NUMBER: 1984:407785 CAPLUS
DOCUMENT NUMBER: 101:7785
TITLE: Purification of methacrylic acid
PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKOXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 59048437	A2	19840319	JP 1982-158824	19820914
JP 03003645	B4	19910121		
PRIORITY APPLN. INFO.:			JP 1982-158824	19820914

L19 ANSWER 15 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB In the preparation of aminopolyacetic acid alkali salts from a mixture of primary or secondary amines, theor. quantity of HCN, HCHO, and aqueous alkali hydroxide, a mixture of HCN(1) and aqueous HCHO (maintained at -10 to 30°) was added to the reactor and the resulting reaction mixture was heated at 60-150°. Thus, 5% HCN(1) 0.67/min and 30% 37% aqueous HCHO 1.85 part/min was introduced from the bottom of a reactor containing 50% aqueous NaOH 384, H₂O 150, and (H₂NCH₂)₂ 60 parts and maintained at 90° for 3 h to give, after azeotropic distillation of by-product NH₃, 93.0% EDTA Na salt vs. 92.0% yield if the 37% aqueous HCHO was

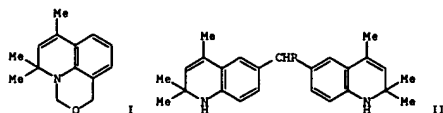
introduced from the top of the reactor sep.
ACCESSION NUMBER: 1983:107774 CAPLUS
DOCUMENT NUMBER: 98:107774
TITLE: Aminopolyacetic acid alkali salts
PATENT ASSIGNEE(S): Nitto Chemical Industry Co., Ltd., Japan
SOURCE: Jpn. Tokkyo Koho, 5 pp.
CODEN: JAXXAD
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 57045425	B4	19820928	JP 1976-102534	19760830
PRIORITY APPLN. INFO.:			JP 1976-102534	19760830

L19 ANSWER 16 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Organic compds. present at >10 µg/mL in 4.5M H₂SO₄ were separated, identified, and determined. These compds. were solubilized from Pb-acid battery separators, made of phenol-formaldehyde resin-impregnated cellulose, by the action 4.5M H₂SO₄ at 75° for 20 h. Separation techniques include: steam distillation, ion-exchange, TLC, gas chromatog., centrifugation, chemical precipitation, paper chromatog., and reverse-phase high-performance liquid chromatog. Identification and quantitation involved the use of gas chromatog., IR, NMR, UV-visible and "total carbon" anal. Glucose, formaldehyde, acetic acid, and formic acid are among the many products found in the leach acid.

ACCESSION NUMBER: 1979:482595 CAPLUS
DOCUMENT NUMBER: 91:82595
TITLE: Analysis of 4.5 mol/L sulfuric acid for organic compounds leached from battery separators
AUTHOR(S): Laird, Edwin C.; Hanna, Samir B.
CORPORATE SOURCE: Globe-Union Inc., Milwaukee, WI, 53201, USA
SOURCE: NBS Special Publication (United States) (1979), 519(Trace Org. Anal.: New Front. Anal. Chem.), 797-802
CODEN: XNBSAV; ISSN: 0083-1883
DOCUMENT TYPE: Journal
LANGUAGE: English



AB The condensation products of 2,2,4-trimethyl-1,2-dihydroquinoline with HCHO (e.g., I and II (R = H)) and MeCHO (e.g., II (R = Me)) were separated by liquid chromatog. and identified by off-line mass spectroscopy. To avoid secondary reactions the chromatog. eluate was thinly spread over glass wool or over the walls of a glass vessel, vacuum evaporated, and then steam distilled into the mass spectrometer at 10-15 torr. The 400-500 mol.-weight products were steam distilled at 10-5 torr without decomposition.

ACCESSION NUMBER: 1979:439285 CAPLUS
DOCUMENT NUMBER: 91:39285
TITLE: Separation and investigation of some heat-sensitive high molecular weight compounds. A combined application of liquid chromatography and mass spectrometry
AUTHOR(S): Fekete, Jenő; Balla, József
CORPORATE SOURCE: Budapesti Musz. Egy., Budapest, Hung.
SOURCE: Magyar Kémiai Folyóirat (1979), 85(3), 104-11
CODEN: MGKFA3; ISSN: 0025-0155
DOCUMENT TYPE: Journal
LANGUAGE: Hungarian

L19 ANSWER 18 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
AB Lacquer binders were prepared by the reaction of epoxy resins with Mannich bases (prepared from bisphenol A [80-05-7], secondary amines, and HCHO [50-00-0]) and used in electrophoretic coating compns. Thus, a mixture of bisphenol A 1100, diethanolamine [111-42-2] 833.5, bis(2-methoxyethyl)amine [111-95-5] 411.5, and 2-propanol 375 parts was treated slowly with 921 parts 40% formalin, and 2-propanol and water were distilled to prepare a Mannich base (92.5% solids) which (2473 parts) was treated with 57 parts paraformaldehyde at 70°, treated (500 parts) at 60° with 95 parts bisphenol A-epichlorohydrin copolymer [25068-38-6] and 36 parts Epikote 162 [30973-88-7] in 60 parts 1,2-dimethoxyethane, mixed with 18 parts AcOH and 1 l. water to give a 35% resin solution, mixed (810 parts) with 30 parts 50% polyacrylate, used for electrophoretic coating, and baked at 180° for 20 min. to give coatings resistant to salt spray.

ACCESSION NUMBER: 1975:517206 CAPLUS
DOCUMENT NUMBER: 83:117206
TITLE: Lacquer binders
INVENTOR(S): Kempton, Fritz E.; Spoor, Herbert
PATENT ASSIGNEE(S): BASF A.-G., Fed. Rep. Ger.
SOURCE: Ger. Offen., 17 pp. Addn. to Ger. Offen. 2,357,075.
CODEN: GWXKXK
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2320301	A1	19750410	DE 1973-2320301	19730421
DE 2320301	C3	19791004		
DE 2320301	B2	19790208		
ZA 7402466	A	19750528	ZA 1974-2466	19740418
BE 813979	A1	19741021	BE 1974-143437	19740419
NL 7405364	A	19741023	NL 1974-5364	19740419
NL 158539	B	19781115		
FR 2226445	A1	19741115	FR 1974-13742	19740419
FR 2226445	B1	19790216		
BR 7403157	A0	19741203	BR 1974-3157	19740419
AT 7403279	A	19760515	AT 1974-3279	19740419
AT 354480	B	19760125		
GB 1457932	A	19761208	GB 1974-17195	19740419
IT 1011253	A	19770120	IT 1974-50504	19740419
SE 409334	C	19791122	SE 1974-5336	19740419
SE 409334	B	19790813		
ES 425531	A1	19760601	ES 1974-425531	19740420
JP 50013499	A2	19750212	JP 1974-44617	19740422
JP 57031574	B4	19820706		

PRIORITY APPLN. INFO.: DE 1973-2320301 A 19730421

AB The waste water containing HCHO and PhOH was passed through a solvent extractor to remove PhOH, mixed with apprx.4-6 moles NH₃ per mole of the residual HCHO, fed into a primary condenser to remove the excess water as vapor, mixed with 1/6-1/2 mole PhOH per mole of the residual HCHO and fed together with mother liquors produced in the following processes into a crystallizer. The adduct crystals produced were separated and taken out, while the mother liquors were fed into a secondary condenser to take out sludges and returned to the crystallizer, while the distd. liquids from the secondary condenser were returned to the solvent extractor. The staining materials were completely recovered.

ACCESSION NUMBER: 1975:484466 CAPLUS
DOCUMENT NUMBER: 83:84466
TITLE: Treatment of waste water in manufacturing processes for phenol resins
INVENTOR(S): Sawabe, Teruo; Kurachi, Teruo
PATENT ASSIGNEE(S): Sumitomo Bakelite Co., Ltd.
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKKXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 49128092	A2	19741207	JP 1973-40041	19730410
			JP 1973-40041	A 19730410

PRIORITY APPLN. INFO.:

AB Liquid or low m.p. solid methylene-bridged polyarylamines with a large proportion of 2,2' and 2,4' links, useful as curing agents in thermoset or thermoplastic polyurethane cast plastics, were manufactured from secondary or tertiary arylamines and formaldehyde [50-00-0] without catalyst or with a weak acid catalyst at >120.deg.. Thus, 3.75 parts NaCl was added to a mixture of 428 parts N-methylaniline [100-61-8] and 81.1 parts 36.5% aqueous tech. HCHO which was polymerized 6 hr at 192-6.deg.. A brown oil was isolated containing .sim.66%

N,N'-dimethyldiaminodiphenylmethanes and formaldehyde -N-methylaniline copolymer. The distillate from the oil at 0.8 mm and b.p. 195-210.deg. was a yellow oil containing 2,2'-bis(N-methylamino)diphenylmethane, 2,4'-bis(N-methylamino)diphenylmethane, and 4,4'-bis(N-methylamino)diphenylmethane in a 1:5.5:13.8 ratio.

ACCESSION NUMBER: 1974:404352 CAPLUS
DOCUMENT NUMBER: 81:4352
TITLE: Methylene bridged polyarylamines
INVENTOR(S): Brooks, Martin Frederick; Kerrigan, Vincent
PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
SOURCE: Brit., 10 pp.
CODEN: BROKAA
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 1341018	A	19731219	GB 1970-10428	19710419
			GB 1970-10428	A 19710419

PRIORITY APPLN. INFO.:

L19 ANSWER 21 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The title compds. were prepared by reaction of acetylureas with HCHO and secondary amines in a refluxing solvent. The yield of product was increased and reaction time was reduced by refluxing the reactants in a hydrocarbon such as C6H6 and removing H2O by distillation

ACCESSION NUMBER: 1973:42003 CAPLUS
 DOCUMENT NUMBER: 79:42003
 TITLE: Aminomethyl derivatives of acetylureas
 INVENTOR(S): Pylaeva, O. E.; Mamaev, V. P.
 PATENT ASSIGNEE(S): Novosibirsk Institute of Organic Chemistry
 SOURCE: U.S.S.R. From: Otkrytiya, Izobret., Prom. Obraztsey, Tovarnye Znaki 1973, 50(16), 50.
 CODEN: UROKAF

DOCUMENT TYPE: Patent
 LANGUAGE: Russian
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
SU 375288	T	19730323	SU 1971-1690479	19710804
PRIORITY APPLN. INFO.:			SU 1971-1690479	A 19710804

L19 ANSWER 22 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The continuous preparation of oligomers (d.p. 2-5) by formaldehyde (50-90-0) condensation with primary or secondary amines I (R1 = H, o-Me, p-CH2C6H4NH2-p; R2 = H, Me, Et) was achieved by separating the HCl-catalyzed condensation product into 1:1, 5:1, or 1:3 side stream-main stream portions, the side stream being recycled at .1eq.40.deg. to be mixed with fresh catalyst and amine and the main stream being carried to final condensation at 80-200.deg.. Thus, aniline (II) [62-53-3] and HCl (2.32:1 II-HCl mole ratio) were cooled to 15.deg., condensed with CH2O (2:1 II-CH2O mole ratio), and the product equally separated into the side stream (.1eq.25.deg.) and main stream. The main stream(.1eq.40.deg.) was heated to 100-2.deg., treated with NaOH at 110.deg. and distilled at 100-230.deg. to give 89% oligomer mixture (d.p. = 2-4). I mixture was treated with phosgene to give polyisocyanate mixts.

ACCESSION NUMBER: 1973:136977 CAPLUS
 DOCUMENT NUMBER: 78:136977
 TITLE: Aromatic polyamines
 INVENTOR(S): Eifler, Willi; Raue, Roderich; Rohe, Ernst Heinrich; Finkel, Josef
 PATENT ASSIGNEE(S): Bayer A.-G.
 SOURCE: Ger. Offen., 20 pp.
 CODEN: GWXKEX

DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2127263	A1	19730104	DE 1971-2127263	19710602
US 3931320	A	19760106	US 1972-256036	19720523
GB 1371960	A	19741030	GB 1972-24940	19720526
IT 958138	A	19731020	IT 1972-50592	19720530
BE 784217	A1	19721130	BE 1972-118123	19720531
NL 7207358	A	19721205	NL 1972-7358	19720531
BR 7203539	A0	19730531	BR 1972-3539	19720531
ES 403366	A1	19750416	ES 1972-403366	19720531
FR 2140224	A1	19730112	FR 1972-20008	19720602
AU 7243590	A1	19740103	AU 1972-43590	19720619
PRIORITY APPLN. INFO.:			DE 1971-2127263	A 19710602

L19 ANSWER 23 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB The title compns. consist mainly of methylenedianilines in which 4-50% of the NH2 groups are substituted with Cl-8 primary or secondary alkyl groups, and are prepared by condensing mixts. of N-alkylanilines and PhNH2 with HCHO in the presence of an acid or by the reductive alkylation of methylenedianilines. Thus, 210 g Tonox (I), a com. mixture containing 4,4'-methylenedianiline (II) 56, 2,4'-methylenedianiline 14, 2,2'-methylenedianiline 2, and higher functional diphenylmethane bases 28 weight %, was mixed with 14.5 g acetone, 75 ml MeOH, and 3.0 g 5% Pt sulfide/C and heated 1.75 hr at 95° and 485-900 psig H. The reaction mixture was cooled, filtered, and evaporated to give 213 g of a brown oil which solidified to a product which melted over a broadrange, becoming completely clear at 50° and in which 12.5% of the primary amino groups were alkylated to isopropylamino groups. The product (29.6 g) was melted and mixed with 100 g Epon 828, deaerated, and hardened 2 hr at 80° and 3 hr at 150° to give a molding with heat deformation temperature (ASTM D648-56) 152°. In another type of preparation, a mixture of PhNH2 167.4, iso-PrNHPh27.0, and 37% HCHO 46.9 g was heated 3 hr at 65°, separated, and the organic layer mixed with 7 ml concentrated HCl and dried by azeotropic distillation at 110° for 6 hr. The mixture was then neutralized, washed, steam distilled to remove excess amines, and the residue dried to give a brown oil, which cured Epon 828 to a heat deformation temperature of 143°. Curing agents were also prepared by reductive alkylation of I with HCHO, PhCHO, iso-BuCOMe, and 2-octanone, and of II with HCHO, acetone, MeCOEt, and iso-Bu-COMe. These compns., liqs. or low melting solids, are easily incorporated into epoxy resins.

ACCESSION NUMBER: 1970:79905 CAPLUS
 DOCUMENT NUMBER: 72:79905
 TITLE: Partially N-alkylated diphenylmethane bases as resin hardeners
 INVENTOR(S): Sundholm, Norman K.
 PATENT ASSIGNEE(S): Uniroyal, Inc.
 SOURCE: Ger. Offen., 24 pp.
 CODEN: GWXKEX

DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1937937		19700129		
FR 2014715			FR	
GB 1273371			GB	
US 3634275		19720000	US	
ZA 6904547		19690000	ZA	
PRIORITY APPLN. INFO.:			US	19680725

L19 ANSWER 24 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB N,N-Dimethylamino alcs. are prepared by replacing each of the hydrogens of the amino group with a Me radical by treating the alc. with at least 3 moles of HCHO/mole amine. The process also includes the selective production of N,N-dialkylamino alcs. such as N,N-dimethylamino alcs. and isomers using different aldehydes, by controlling the reaction mixture to remove HCO2H prior to separation of the methylated amino alc. or to ensure the presence of HCO2H. Dialkylamino primary and secondary alcs. are converted to dialkylamino secondary and tertiary alcs, resp. Thus, Me2C(NH2)CH2OH and HCHO introduced into a bomb and rocked 4 hrs. at temps. ranging from 114-126° to 160-3° and the product dehydrated by azeotropic distillation with PhMe and fractionated gave 69.2 to 81.0% yields of Me2C(NMe2)CH2OH (I). I (109 g., 95.5%), 100 ml. H2O, 1 ml. HCO2H, and 100 ml. PhMe distilled through a column, freed from H2O, and fractionated yielded 70% Me2C(OH)CH2NMe2. EtCH(NMe2)CH2OH distilled with 3 weight % HCO2H 8 hrs. gave 44% EtCH(OH)CH2NMe2. In the production of N,N-dialkylamino alcs. by reacting an amino alc. with an aldehyde and separating the N,N-dialkylamino alc. from the mixture, the addition of a strong base to the mixture prior to the separation neutralizes the HCO2H present and thus reduces the production of isomers.

ACCESSION NUMBER: 1968:505983 CAPLUS
 DOCUMENT NUMBER: 69:105883
 TITLE: N,N-Dimethylamino alcohols from formaldehyde and amino alcohols
 INVENTOR(S): Tindell, John B.
 PATENT ASSIGNEE(S): Commercial Solvents Corp.
 SOURCE: U.S., 5 pp.
 CODEN: USXXAM

DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3402203	A	19680917	US 1964-412301	19641119
PRIORITY APPLN. INFO.:			US 1964-412301	A 19641119

L19 ANSWER 25 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Gaseous mixts. of an olefin, HCHO, and H₂O₂, such as produced by partial oxidation of hydrocarbons, preferably C₃H₈ and C₄H₁₀, are separated by extractive distillation with AcOH to give: (1) a gaseous overhead product containing HCHO and olefin, and (2) a bottom product consisting of a solution of H₂O₂ in AcOH. The dissolved H₂O₂ in the latter solution can then be converted to AcOOH in the presence of an acid catalyst. The extractant used may also consist of ethers, esters, cyclic acetals, and other carboxylic acids provided they are free of primary and secondary OH groups, inert to H₂O₂, and will dissolve at least 5% H₂O₂ at 70°. Thus, a mixture of 26.4 millimoles/min. C₃H₈ and 3.79 millimoles/min. O were reacted continuously at 468-71°, consuming 7% of the C₃H₈ and 62% of the O. This yielded a gaseous product in which, of the C₃H₈ consumed, 64% was converted to C₃H₆, 13% to C₂H₄, 6% to C oxides, 2% to H₂O₂, 4% to oxygenated C₃ products, and 10% to liquid products, largely MeOH. H₂O₂ was produced at the rate of 0.2 part by weight per part C₃H₈ consumed. The oxidation mixture was then passed into a plate column equipped with a thermosiphon reboiler and a reflux condenser operating at 10° under a pressure of approx. 150 mm. Extractant consisting of HOAc was fed into the column head at 84 ml./hr. and the column base temperature was kept at 70°. After 1 hr., overhead product contained approx. 0.44 g. HCHO, 2 g. C₃H₆, 0.01 g. peroxy acetyl, and 66 g. C₃H₈. Bottom product weighed 63.4 g. and contained 0.74 g. H₂O₂ and 0.03 g. HCHO, the remainder being HOAc containing 2% H₂O. The latter solution was vacuum concentrated to 10% H₂O₂, mixed with 2% p-toluenesulfonic acid, and passed into a vacuum concentrating column at 31 mm. to yield a HOAc-H₂O₂-HOAc distillate containing approx. 22% HOAc.

ACCESSION NUMBER: 1968:495975 CAPLUS

DOCUMENT NUMBER: 69:95975

TITLE:

Separation of formaldehyde from hydrogen peroxide and preparation of peracetic acid

MacLean, Alexander F.; Hobbs, Charles C.

Calanese Corp.

U.S., 6 pp.

CODEN: USXXAM

Patent

English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3398185	A	19680820	US 1966-571975	19660812
PRIORITY APPLN. INFO.:			US 1966-571975	A 19660812

L19 ANSWER 26 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB A mass spectrometric study of the reaction between gaseous HCHO (also HCDO and DCDO) produced by the distillation of the corresponding polyoxymethylenes and O(3P) atoms produced by NO titration of N-atoms generated with a microwave discharge in mol. N at 1.5 torr. was carried out. The reaction was studied at low concns. and low conversion of the HCHO with excess O atoms, and was 1st order with respect to O atoms and HCHO. A rate constant was obtained. Atomic H, H₂O, mol. O, and CO₂ were identified as reaction products and their formation was explained by reaction O + HCHO = OH + CHO (1), as suggested by Geib (CA 31, 20564), followed by the fast secondary reactions CHO + O = CO₂ + H, CHO + OH = H₂O + CO, and OH + O = O₂ + H. No support for Avramenko and Lorentso's suggested primary reaction step (CA 47, 9728g) O + HCHO = CO + H₂O was obtained. The activation energy for (1) is 5.5 kcal./mole.

ACCESSION NUMBER: 1967:79980 CAPLUS

DOCUMENT NUMBER: 66:79980

TITLE: Reaction of O(3P) atoms with formaldehyde

Niki, Hiromi

Ford Motor Co., Dearborn, MI, USA

Journal of Chemical Physics (1966), 45(6), 2330-2

CODEN: JCP5A6; ISSN: 0021-9606

Journal

English

LANGUAGE:

L19 ANSWER 27 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB The reaction of HC.tpbend.CCRR10H (I) with R₂CHO under anhydrous conditions, yields first an acetylenic glycol, which on alkaline cleavage gives a ketone or aldehyde and a primary or secondary acetylenic alc. In an example, 168 g. I (R = R₁ = Me), 70 g. anhydrous paraformaldehyde, 60 g. of catalyst consisting of 12% Cu acetylide on activated C, and 200 cc. CH₂(OMe)₂ was charged to a rocking bomb, heated 30 hrs. at 105°, cooled, and filtered and the filtrate fractionally distilled to give 95.5% 2-methyl-3-pentyn-2,5-diol (II). II(95 g.) was cleared by heating at 175°/300 mm. with 0.5 g. K₂CO₃ for 5.75 hrs. to yield 71 g. yellow liquid, containing Me₂CO and propargyl alc. (III), b. 116-17°. Similarly 3-methyl-1-nonyn-3-ol gave 50% 4-methyl-2-decyne-1,4-diol (IV), b. 112°. Cleavage of IV with K₂CO₃ gave anhydrous III and 2-octanone.

ACCESSION NUMBER: 1964:15976 CAPLUS

DOCUMENT NUMBER: 60:15976

ORIGINAL REFERENCE NO.: 60:2765a-c

TITLE: Acetylenic glycols

Leeds, Morton W.; Russell, James P.; Vitcha, James F.

Air Reduction Co., Inc.

3 pp.

Patent

Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3108140	---	19631022	US	19591231

L19 ANSWER 28 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN

AB Heavy residues formed during the condensation of CH₂O and monoolefins are converted to highly hydroxylated compds. for use as commercial solvents, antigels, plasticizers for paints and varnishes, and hydraulics. The heavy residue is treated with a low mol. weight of alc. of not more than 4 C atoms, preferably in a 10% ratio. The reaction is catalyzed by an inorg. or an organic acid or an acid salt. High purity is not required for either the alc. or the acid. One to 10% by weight of acid is usually added to the residue. The reaction may be carried out at 30 to 100° preferably from 50 to 80°. Usually the reaction is conducted batchwise in a heated flask equipped with a reflux condenser. On completion of the reaction, the products are separated and recovered by distillation, azeotropic distillation, extraction or ion exchange. In a typical example, 2 kg. residue reacted with 315 kg. methanol in 74 g. H₂SO₄ to give 975 g. methylal, having a primary and secondary hydroxyl index of 460 and a tertiary hydroxyl index of 380.

ACCESSION NUMBER: 1963:454292 CAPLUS

DOCUMENT NUMBER: 59:54292

ORIGINAL REFERENCE NO.: 59:9801d-e

TITLE: Hydroxy hydrocarbons from residues of the manufacture

of conjugated diolefins

Auffray, Robert; Davidson, Mircea; Jenny, Robert

Institut Francais du Petrole, des Carburants et

Lubrifiants

14 pp.

Patent

Unavailable

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
FR 1313721	---	19630104	FR	19600420

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 909673		19621031	GB	
PRIORITY APPL. INFO.:			CA	19600611

after reaction with HCHO is given.
ACCESSION NUMBER: 1962:483904 CAPLUS
DOCUMENT NUMBER: 57:43904
ORIGINAL REFERENCE NO.: 57:16817b-1, 16818a-e
TITLE: Characteristic cross-links during the reaction of collagen with formaldehyde in an acid medium
AUTHOR(S): Rosmus, Jan; Dayl, Zdenek
CORPORATE SOURCE: Central Res. Inst. Food Ind., Prague
SOURCE: Kozarstvi (1962), 12, 99-101
CODEN: KOZAA7; ISSN: 0023-4338
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

ACCESSION NUMBER: 1963:30935 CAPIUS
DOCUMENT NUMBER: 58:30935
ORIGINAL REFERENCE NO.: 58:5190b-e
TITLE: Nuclear fission in synthesizing organic compounds
INVENTOR(S): Conner, Willard P. (Jr.) Davis, William E.
PATENT ASSIGNEE(S): Hercules Powder Co.
SOURCE: 8 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3065159		19621120	US	19571217

obtained given): 2,4-HeC₂Gh₃NNH₂ (II), CH₂O (II), 40 h., 40, needles, 118° (MeOH); 1. BzH (III), 15 min., 70, -, -, -, 0-2NC₂Gh₄CHO (IV) 5 min., 60, ruby-red needles, 141-2° (AcOH); 1. m-ON₂C₂Gh₄CHO (V) 5 min., 90, red prisms, 185-6° (AcOH); 1. p-ON₂C₂Gh₄CHO (VI), 5 min., 75, dark red prisms, 171-2° (AcOH); 1. p-MeC₂Gh₃NNH₂CHO (VII), 10 min., 90, leaflets, 139-41° (90% AcOH); 1. PhCH₂CH₂CHO (VIII), 60 min., 15, -, -, -, 1, o-HOC₂Gh₄CHO (IX), 10 h., 55, -, -, -, 1. AcPh (X), 24 h., 30, light brown needles, 89-90° (EtOH) (decomposed within a few hrs.); 1. cyclohexanone (XI), -, -, -, 2,4-Br₂C₂Gh₃NNH₂ (XII), 11, -, -, -, 1. XI, -, -, -, 1. XI, -, -, -, 1. XI, 96 h., 50, gold-yellow leaflets, 90-102° (EtOH); XII, VI, 60 min., 70, orange needles, 134-5° (EtOH); XII, VII, -, -, -, 1. XII, VIII, -, -, -, 1. XII, IX, -, -, -, 1. XII, X, -, -, -, 1. XII, XI, -, -, -, 1. XII, XII, -, -, -, 2,4-Br₂C₂Gh₃NNH₂ (XIII), 11, -, -, -, 1. XIII, 11, 10 h., 45, -, -, -, 1. XIII, IV, 10 min., 85, -, -, -, 1. XIII, V, 5 min., 60, -, -, -, 1. XIII, VI, 8 min., 65, -, -, -, 1. XIII, VII, 60 min., 65, prisms, 124-5° (EtOH); XIII, VIII, 5 min., 75, -, -, -, 1. XIII, IX, 24 h., 55, -, -, -, 1. XIII, X, 60 h., 35, needles, 64-5° (decomposed within a few hrs.); XIII, XI, -, -, -, 1. 2,4-Br₂C₂Gh₃NNH₂ (XIV), 11, -, -, -, 1. XIV, 11, 2 min., 90, gold-yellow needles, 116° (EtOH); XIV, V, 1 min., 90, gold-yellow needles, 134-5° (EtOH); 1:1 CHCl₃-EtOH; XIV, VI, 1 min., 100, gold-yellow needles, 158° (1:1 CHCl₃-EtOH); XIV, VII, 15 min., 100, pale yellow leaflets, 137-8° (1:5 CHCl₃-EtOH); XIV, VIII, -, -, -, 1. XIV, IX, 15 min., 85, needles, 79-80° (EtOH); XIV, X, -, -, -, 1. XIV, XI, -, -, -, 1. 2,4-Br₂C₂Gh₃NNH₂ (XV), 11, -, -, -, 1. XV, 13, 35 min., 70, -, -, -, 1. XV, 10 min., 100, -, -, -, 1. XV, V, 1 min., 85, -, -, -, 1. XV, VI, 1 min., 90, -, -, -, 1. XV, VII, 10 min., 100, pale yellow needles, 173-5° (AcOH); XV, VIII, 1 min., -, -, -, 1. XV, IX, 5 h., 20, -, -, -, 1. XV, X, 8 h., 40, needles, 63° (EtOH) (decomposed within a few hrs.); XV, XI, -, -, -, 1. 2,4-Br₂C₂Gh₃NNH₂ (XVI), 11, -, -, -, 1. XVI, 11, -, -, -, 1. XVI, IV, 1 h., 85, orange needles, 102° (EtOH); XVI, V, 5 min., 80, gold-yellow needles, 117-18° (EtOH); XVI, VI, 3 min., 85, orange needles, 145° (1:5 CHCl₃-EtOH); XVI, VII, 10 h., 90, light yellow leaflets, 95° (EtOH); XVI, VIII, -, -, -, 1. XVI, IX, 2 min., 85, needles, 68-9° (EtOH); XVI, X, -, -, -, 1. XVI, XI, -, -, -, 1. 2,4-Br₂C₂Gh₃NNH₂ (XVII), 11, -, -, -, 1. XVII, 11, 1 min., 60, -, -, -, 1. XVII, IV, 40 min., 70, -, -, -, 1. XVII, V, 1 min., 45, -, -, -, 1. XVII, VI, 5 min., 60, -, -, -, 1. XVII, VII, 1 h., 70, prisms, 156° (AcOH); XVII, IX, 5 min., 75, pale yellow needles, 162-3° (AcOH); XVII, IX, 15 s., 90, needles, 154-5° (AcOH); XVII, X, 3 h., 70, prisms, 86 (decomposed within a few hrs.); XVII, XI, 5 s., 60, leaflets, 60-1° (EtOH); 2,4-Br₂C₂Gh₃NNH₂ (XVIII), 11, -, -, -, 1. XVIII, 11, 5 s., 55, needles, 90-1° (MeOH); XVIII, IV, 5 s., 80, needles, 159-60° (EtOH); XVIII, V, 5 s., 80, needles, 169-70° (PrOH); XVIII, VI, 5 s., 20, needles, 190° (EtOH); XVIII, VII, 5 s., 85, prisms, 117° (MeOH); XVIII, VIII, 5 s., 85, needles, 91-2° (EtOH); XVIII, IX, 5 s., 75, needles, XVIII, X, -, -, -, 1. XVIII, XI, -, -, -, 1. 4,3-Br₂C₂Gh₃NNH₂ (XIX), 11, -, -, -, 1. XIX, 11, 10 min., 55, prisms, 126° (EtOH); XIX, IV, 30 min., 60, ruby-red prisms,

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175° (decompn.) (AcOH); XIX, V, 30 min. 85, orange-red prisms, 152-3° (AcOH); XIX, VI, 5 min., 100, ruby-red leaflets, 174-6° (AcOH); XIX, VII, 5 min., 75, leaflets, 161-3° (decompn.) (AcOH); XIX, VIII, 1 min., 70, yellowish leaflets, 143-4° (EtOH); XIX, IX, 4 min., 80, leaflets, 163-4° (decompn.) (AcOH); XIX, X, 4 h., 15, leaflets, 102-4° (EtOH) (decompd. within a few hrs.); XIX, XI, -, -, -, 4,3-BrMeC6H3NMeNH2 (XX), II, -, -, -, XX, XII, 5 s., 85, light yellow needles, 130° (EtOH); XX, IV, 5 min., 60, red needles, 131° (EtOH); XX, V, 12 min., 60, orange-red needles, 138-9° (3:1 EtOH-CHCl3); XX, VI, 2 min., 80, orange-red leaflets, 185-6° (1:1 EtOH-CHCl3); XX, VII, 24 h., 80, pale yellow needles, 146-7° (3:1 EtOH-CHCl3); XX, VIII, 5 s., 85, pale yellow needles, 143-4° (EtOH); XX, IX, 1 min., 85, pale yellow leaflets, 111° (EtOH); XX, X, -, -, -, XX, XI, -, -, -, 3,4-BrMeC6H3NMeNH2 (XXI), II, -, -, -, XXI, III, 2 h., 35, leaflets, 119-21° (50% EtOH); XXI, IV, 5 min., 85, red prisms, 167-8° (AcOH); XXI, V, 5 min., 85, orange prisms, 146-8° (EtOH); XXI, VI, 20 min. 60, red-brown needles, 150-1° (EtOH); XXI, VII, 1 min., 95, pale yellow prisms, 189-90° (1:1 EtOH-AcOH); XXI, VIII, 1 min., 65, pale yellow prisms, 128° (25% EtOH); XXI, IX, 5 min., 80, needles, 166° (25% EtOH); XXI, X, 45 min., 65, leaflets, 82-4° (EtOH) (decompd. within a few hrs.); 3,4-BrMeC6H3NMeNH2 (XXII), II, -, -, -, XXII, III, 5 s., 65, leaflets, 89-90° (EtOH); XXII, IV, 1 min., 60, orange needles, 138-9° (1:3 CHCl3-EtOH); XXII, V, 10 min., 80, red leaflets, 133-4° (1:3 CHCl3-EtOH); XXII, VI, 30 s., 70, orange needles, 178° (1:3 CHCl3-EtOH); XXII, VII, 2.5 h., 60, pale yellow needles, 147° (1:3 CHCl3-EtOH); XXII, VIII, 30 s., 75, pale yellow leaflets, 99-100° (1:3 CHCl3-EtOH); XXII, IX, 30 s., 90, leaflets, 119° (1:3 CHCl3-EtOH); XXII, X, -, -, -, XXII, XI, -, -, -, VI (375 mg.) and 305 mg. IX in 7 cc. EtOH treated with 600 mg. XII in 3 cc. EtOH and kept 24 h. at room temp. yielded 480 mg. deriv. of VI. a,2,4-Trimethylphenylhydrazones (280 mg.) of VI in 2.5 cc. concd. H2SO4 kept 1.5 h. at room temp., poured into 50 cc. iced H2O, and filtered after several hrs. gave 97 mg. VI, m. 106°. IX (305 mg.) and 250 mg. XI in 5 cc. EtOH treated with 800 mg. XXII in 3 cc. EtOH and filtered after 8-10 h. gave 640 mg. deriv. of IX. 3-Bromo- α ,4-dimethylphenylhydrazones (640 mg.) of IX in 10 cc. EtOH and 10 cc. concd. HCl refluxed 0.5 h., cooled, dild. with H2O, steam distd., and the distillate extd. with Et2O gave 170 mg. IX.

ACCESSION NUMBER: 1962:73214 CAPLUS
DOCUMENT NUMBER: 56:73214
ORIGINAL REFERENCE NO.: 56:14125h-1,14126a-1,14127a-c
TITLE: Condensation of carbonyl compounds with hydrazines. V. The reaction of aldehydes and ketones with disubstituted phenylhydrazines and their α -methyl derivatives
AUTHOR(S): Stroth, Hans Hartwig; Nikolaiewski, Hans Edmund
CORPORATE SOURCE: Humboldt Univ., Berlin
SOURCE: Chemische Berichte (1962), 95, 562-70
CODEN: CHBERM; ISSN: 0009-2940
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 56:73214

L19 ANSWER 33 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)

191, 63-77
CODEN: CDXKAN; ISSN: 0577-6848
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 33 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
AB The addition reactions of d-limonene (I) with HCHO (II), MeCHO, EtCHO, and R2NH as well as the preparation of limonenylcarbinol derivs. were described. A mixture of 20 g. I, 4.5 g. II, and 10 g. EtOH was sealed in a glass tube and heated at 200-20° for 12 hrs. to give 2.8 g. (III) limonenylcarbinol (III), b4 102-5°, d8 0.9612, nD20 1.5069, phenylurethan m. 54-5°. I (45.3 g.), 10 g. II and 20 g. Ac2O at 180-90° for 5 hrs. in an autoclave gave 29.64 limonenylmethyl acetate (IV), b4 96-106°, d20 0.9618, nD20 1.4790. Saponification of IV (13 g.) with 6 g. KOH at 180° 4 hrs. gave 964 1,8(9)-p-menthadien-10-ylcarbinol (V), b4 102-6°, d17 0.9603, n17D 1.5020; phenylurethan m. 56-7°. Reduction of 3.93 g. V in MeOH with Pd-BaSO4 containing 3% Pd gave 3 g. 1-p-menthen-10-ylcarbinol (VI), b4.5 100-3°, n13D 1.4923. To a cooled mixture (-5°) of 12 g. 1-p-menthene, 3 g. II, 17 g. 95% AcOH, and 4 g. Et2O a mixture of 7 g. 95% AcOH and 2.5 g. 98% H2SO4 was added, stirred for 5 hrs. after standing at room temperature overnight, extracted with Et2O to give 3 g. 1(2)-p-menthen-6-ylmethyl acetate (VII), b4 90-100°, nD 1.4860. Saponification of VII with KOH gave the corresponding carbinol, b3 95-7°, nD 1.4896. II and III heated at 150-70° for 6 hrs. gave formaldehyde mono-1,8(9)-p-menthadien-10-yl acetal (VIII), b5 155-162°, n20.5D 1.5066, d20.5 1.306. The esters of III with maleic, phthalic, and succinic acids were prepared. Employing palmitoyl, capryloyl, isovaleryl, phenylacetyl, and cinnamoyl chloride, III gave esters of the corresponding acids. To a mixture of 4 g. CrO3, 5 ml. H2O, and 100 ml. AcOH, a mixture of 9 g. III, 30 ml. Me2CO, and 20 ml. AcOH was added in 25 min. at 50-5° with stirring, after 4.5 hrs. the mixture poured into H2O, extracted with Et2O, and fractionally distilled to give 3.5 g. 3-(4-methyl-3-cyclohexen-1-yl)-3-buten-1-ol (IX), b4 88° nD 1.5045; 2,4-dinitrophenylhydrazones (DNP) m. above 220° semicarbazone m. 192°. III (5 g.) with 18.5 g. Al[OCH(Me)]2 in 150 g. Me2CO and 150 g. anhydrous C6H6 refluxed for 40 hrs. gave 1 g. 6-(4-methyl-3-cyclohexen-1-yl)-3,5-heptadien-2-one (X), b3 125-33°, n10D 1.5271, λ 295 m μ , ϵ 4480, λ 223 m μ , ϵ 3340; DNP m. 179-80°, pos. iodoform reaction. Similarly, III and MeCOEt gave 7-(4-methyl-3-cyclohexen-1-yl)-4,6-octadien-3-one (XI), b2 125-132°, n23D 1.4806, λ 291 m μ , ϵ 6650, λ 225 m μ , ϵ 4340, neg. iodoform reaction; DNP m. 203°. Me, Et, PhCH2, and allyl ethers of III were prepared and their b.p., nD, d24, λ yield given: Me, b12 85-6°, 1.4870, 0.9317, 80; Et, b4 96-7°, 1.4921, 0.9353, 90; allyl, b17 115-18°, 1.4927, 0.9293, 80; PhCH2, b10 175-9°, 1.5300, 0.9885, 90. I (34 g.), 1.5 g. EtCHO, and 1 g. ZnCl2 gave 6-propyldiene-1,8(9)-p-menthadiene, b3 130-6°, n17D 1.5130, d17 0.9200, λ 224 m μ , ϵ 4220, while the treatment in AcOH with a catalytic amount of H2SO4 gave cyclic ether, b0.5 110-14°, n16D 1.4970, d15 0.9734. A mixture of 25 g. Me2NH, 34 g. I, and 5.8 g. II in 60 g. AcOH was refluxed 16 hrs. to give 11% N,N-dimethylimonenylmethylaniline (XIII), b3.5 92-3°, which reacted with Wagner's reagent to give adduct of K4Fe(CN)6. Similarly, Et2NH gave 5% N,N-di-Et derivative of XIII, b3 101°.

ACCESSION NUMBER: 1961:112238 CAPLUS
DOCUMENT NUMBER: 55:112238
ORIGINAL REFERENCE NO.: 55:21159c-1
TITLE: Reaction of limonene with aldehydes
AUTHOR(S): Suga, Kyoichi; Watanabe, Shoji
SOURCE: Kagaku Kenkyu Hokoku (Chiba Daigaku) (1960), 11(No. bound

HCHO was 3%, indicating that some of hydrazine groups were linked to more than 1 HCHO.

ACCESSION NUMBER: 1961:15756 CAPLUS
DOCUMENT NUMBER: 55:15756
ORIGINAL REFERENCE NO.: 55:3105h-1,3106a-b
TITLE: Reversible function resins. I. Preparation and properties of cross-linked poly(methacryloylhydrazine)
AUTHOR(S): Sugihara, Mizuhoro; Okamoto, Nagahisa
SOURCE: Kagaku to Kogyo (Osaka, Japan) (1959), 33, 343-8
CODEN: KKG0AG; ISSN: 0368-5918
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

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AB A reversible function resin, which reversibly takes up or gives up small organic mols., depending on their functional group, was prepared

Cross-linked poly(methacryloylhydrazine) was obtained by treating methyl methacrylate-divinylbenzene copolymer with aqueous 80% solution of hydrazine.

HCHO easily condenses with the resin at 100° and can be taken out by steam distillation in an acidic condition. The optimum content of hydrazine in the resin was 10 cc./g. resin in order to obtain the maximum degree of condensation with HCHO. The amount of HCHO taken up by the resin was 28.3 mg./g. resin when the concentration of HCHO was 9.25% (condensed at 100°, 3 hrs.). This amount was nearly proportional to the HCHO concentration. The condensation was usually accompanied with secondary reactions at higher temps. The analysis of the resin for N content by Dumas' method shows only 1.8%; the N content estimated from the amount of bound

HCHO was 3%, indicating that some of hydrazine groups were linked to more than 1 HCHO.

ACCESSION NUMBER: 1961:15756 CAPLUS
DOCUMENT NUMBER: 55:15756
ORIGINAL REFERENCE NO.: 55:3105h-1,3106a-b
TITLE: Reversible function resins. I. Preparation and properties of cross-linked poly(methacryloylhydrazine)
AUTHOR(S): Sugihara, Mizuhoro; Okamoto, Nagahisa
SOURCE: Kagaku to Kogyo (Osaka, Japan) (1959), 33, 343-8
CODEN: KKG0AG; ISSN: 0368-5918
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

L19 ANSWER 35 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Irradiation of 5.56 millimoles D-mannose (III) in 100 ml. H₂O with a Co60 source to a total energy input of 6.65 + 1022 e.v. gave mannonic (IV) and mannanuronic (V) acids and their 8- and 8-lactones, II, and erythrose (VI). The products were identified by paper chromatography with 4:1:5 BuOH-AcOH-H₂O. Similar conclusions were derived from autoradiographs of paper chromatograms of irradiated solns. of mannose-1-C14. The distillate from irradiated solution contained HCOOH. The extent of formation of acids and H₂O₂ and changes in the ultraviolet spectrum were measured as a function of energy input during the irradiation. Isotope-dilution analysis was used to estimate the products obtained on irradiation of 5.56 millimoles III in 100 ml. H₂O in the presence of O and at a dose rate of 1.60 + 1017 e.v./ml. sec. for 39 hrs.; yields at total energy inputs of 3.7 + 1022 and 2.25 + 1023 e.v., resp., were: III, 3.5, 0.16; II, 0.44, 0.26; D-xylose (VII), 0.06, 0.17; glyoxal, 0.40, 1.40; (HOCH₂)₂CO, 0.05, 0.31; H₂C₂O₄, 0.04, 0.74; HCHO, 0.18, 0.18; sugar acids and VI (estimated from paper chromatography), 0.46, 0.57, and 0.12, 0.69, resp.; CO₂ (determined gravimetrically), 0.03, 2.33; and HCOOH (estimated by titration of the volatile acid), 0.22, 0.34 millimoles. Initial G-values were: for consumption of III, 3.5; and for formation of II, 0.5; H₂CO, 0.3; glyoxal, 0.64; sugar acids, 1.6; and VI, 0.18. Expts. with D-mannose-1-C14 indicated that the primary degradation processes included (a) oxidation to IV and V, (b) direct scission of the 1,2-bond to form II and H₂CO, (c) scission of the 2,3-bond to give 2-carbon fragments and VI, and (d) scission of the hexose to give 3 two-carbon fragments. Secondary processes led to formation of II (from IV), VII (from V), H₂C₂O₄, HCOOH, and CO₂.
 ACCESSION NUMBER: 1961:11669 CAPLUS
 DOCUMENT NUMBER: 55:11669
 ORIGINAL REFERENCE NO.: 55:2252a-e
 TITLE: Radiation chemistry of carbohydrates. VI. Action of γ -radiation on aqueous solutions of D-mannose in oxygen
 AUTHOR(S): Phillips, G. O.; Criddle, W. J.
 CORPORATE SOURCE: Univ. Coll., Cardiff, UK
 SOURCE: Journal of the Chemical Society, Abstracts (1960) 3404-12
 CODEN: JCSAAZ; ISSN: 0590-9791
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 37 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 G1 For diagrams, see printed CA issue.
 AB The base-catalyzed formation of aldols from Me₂CO and CH₂O according to Tollens, as well as the closely connected Cannizzaro reaction was demonstrated by paper chromatographic investigations. To a solution of 4 ml. Me₂CO in 41 ml. 35% formalin was added a solution of 4 g. NaOH in 20 ml. H₂O at 0°. Samples were taken after 0.09, 0.25, 0.5, 1, 2, 3, 18, 24, 42, 48, and 96 hrs., resp., acidified with 2N HCl, 0.003 ml. applied to Whatman Number 1 paper [together with CH₂ClR₂CO.CN₃RM, CH₂O (I, R₁ = R₂ = R₃ = R₄ = CH₂OH) (Ia) (anhydrousheptose) and 3-octobutanol as test compds.], chromatographed (descending) with 6:2:7 BuOH-MeOH-H₂O and developed with Tollens reagent. Ia was found to be one of the main products in the mixture. The degradation of perhydroxymethylated carbonyl systems (e.g. Ia) by inorg. and organic bases as well as by acids, came to a standstill after cleaving one or a maximum of 2 mols. CH₂O. To 0.5 g. Ia in 5 ml. H₂O was added 5 ml. 5N NaOH at 20°; after 2, 15, 30 and 60 min., resp., samples were chromatographed without or with previous acidification. Aided by the relationship of the RM values with the number of OH groups, the degradation products were found to be I (R₁ = R₂ = R₃ = CH₂OH, R₄ = H), I (R₁ = R₃ = CH₂OH, R₂ = R₄ = H), I (R₁ = R₂ = CH₂OH, R₃ = R₄ = H), and (HOCH₂)₃CCOC(CH₂OH)₃. It was demonstrated, that the degradation in the presence of acceptors such as salicylamide, p-aminobenzoic acid, anthranilic acid, 8-naphthol, and acetoacetate, stopped at the same dealdolization stages. This limited reversibility of the aldol formation of carbonyl compds. by CH₂O was explained by an anionotropic effect, which, in presence of Lewis acids, predominated the secondary reaction scheme of the base- and acid-catalyzed aldol reaction and therefore also of the Mannich reaction. This effect was responsible for the nucleophilic exchange of aldol hydroxyls by amine residues under formation of Mannich bases, when the degradation was carried out with organic bases. To 15 g. Ia in 200 ml. H₂O was added 72 ml. piperidine (II), the mixture extracted with Et₂O, and the extract dried and distilled to give 33 ml. dipiperidinomethane, b₁₅ 103-4°. After standing 5 days, the aqueous phase yielded 8 g. 1,1,3,3-tetrakis(piperidinomethyl)acetone (III), m. 112-13° (AcOH), infrared spectrum given. A solution of 5 g. Ia in 25 ml. II was refluxed 1 hr., concentrated in vacuo, and AcOH added to the oil to give 3.5 g. I (R₁ = R₂ = CH₂OH, R₃ = CH₂CNCH₂SH₁₀, R₄ = H), m. 107-8°, infrared spectrum given. The tribenzoate of I (R₁ = R₂ = R₃ = CH₂OH, R₄ = H), m. 172-3°. Ia (6 g.) in 25 ml. II refluxed 7 hrs. yielded 4 g. I (R₁ = R₃ = CH₂CNCH₂SH₁₀, R₂ = R₄ = H), m. 94-5° (AcOEt), infrared spectrum given. I (1 g.), R₁ = R₂ = CH₂OH, R₃ = CH₂CNCH₂SH₁₀, R₄ = H, refluxed 6 hrs. with 5 ml. II, gave I (R₁ = R₃ = CH₂CNCH₂SH₁₀, R₂ = R₄ = H). Heating 0.5 g. I (R₁ = R₂ = CH₂OH, R₃ = CH₂CNCH₂SH₁₀, R₄ = H), with 5 ml. H₂O and 1 ml. II gave III. III was also obtained by heating 0.2 g. I (R₁ = R₃ = CH₂CNCH₂SH₁₀, R₂ = R₄ = H), with 5 ml. H₂O and 1 ml. II. The acid-catalyzed aldol reaction is based on an unknown autocatalysis effect and is explained by an electrophilic addition of CH₂O (in the form of the hydroxy-carbonium cation .sym.CH₂OH) to the polarized enol double bond. The product formation was demonstrated on the system levulinic acid and CH₂O by paper chromatographic techniques and involved compds. such as 3,5,5-tris(hydroxymethyl)dihydrodeoxyxypatulinic acid lactone (IV) diacetate and the dihydroxymethylene ether of IV. Levulinic acid (V) (1.2 g.), 5 ml. AcOH, 0.36 ml. concentrated H₂SO₄, and paraformaldehyde (VI) were refluxed 10 min. (molar ratios V/VI 1:1, 1:2, 1:3, 1:5), 0.7 g. Na₂CO₃ in 10 ml. H₂O was added to each solution, the neutralized solns. applied to 2 Whatman

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 AB The effect of variations in reaction conditions on the nature and amount of the end products in the telomerization of styrene with HCHO in AcOH catalyzed by concentrated H₂SO₄ was examined. 4-Phenyl-1,3-dioxane and 1-phenyl-1,3-propanediol diacetate were isolated by fractional distillation and the average mol. weight of the total product measured by the f.p. depression method in benzene. The average mol. weight of the total product was a function of the formaldehyde-styrene ratio when the catalyst concentration was constant. The degree of polymerization was an almost linear function of the catalyst concentration. A relatively large amount of 4-phenyl-1,3-dioxane is formed in the 1st few min., together with the normal telomerization products. This cyclic formal was split by protolysis in a comparatively slow secondary reaction with styrene; it thus acted as an intermediate formaldehyde donor. A carbonium ion mechanism was suggested for the reaction.
 ACCESSION NUMBER: 1960:103458 CAPLUS
 DOCUMENT NUMBER: 54:103458
 ORIGINAL REFERENCE NO.: 54:19688g-1
 TITLE: Telomerization and Prins reaction of styrene and formaldehyde in acetic acid. Role of cyclic formal in the reaction mechanism
 AUTHOR(S): Heslings, A.
 CORPORATE SOURCE: Plastics Research Inst. T. N. O., Delft, Neth.
 SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (1960), 79, 222-30
 CODEN: RTCFB4; ISSN: 0370-7539
 DOCUMENT TYPE: Journal
 LANGUAGE: English

L19 ANSWER 37 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 AB filter papers, chromatographed (ascending), one paper sprayed with Tollens reagent and the other one with H₂NOH-FeCl₃. Considerable resistance was encountered with the reverse process, the solvolytic cleavage of CH₂O from perhydroxymethylated carbonyl compds. by AcOH-H₂SO₄ and other strong mineral acids. IV (10 g.) in 50 ml. 50% H₂SO₄ was boiled 3 hrs., 180 ml. H₂O added, the mixt. extd. with CHCl₃, and the aq. layer extd. with Et₂O to give 0.3 g. IV dihydroxymethylene ether, m. 160-2° (EtOH). Unchanged IV (1 g.) was recovered from the aq. layer. The Mannich reaction was believed to be a secondary stabilization reaction to the base- and acid-catalyzed aldol reaction, according to expl. conditions. The anionotropic effect explained the fact that in the Mannich reaction (of compds. with several acidic H atoms at the same C atom), one acidic H atom cannot be substituted by the aminomethyl residue but only by a hydroxymethyl group. A special case is presented by carbonyl systems which have only one acidic H atom. Iso-PrCHO (3.6 g.), 6 g. II.HCl and 1 g. VI were refluxed 15 min. with 5 ml. abs. EtOH, 20 ml. H₂O added, the pH adjusted to 1 with 2N HCl, extd. with Et₂O, the Et₂O evapd., and the residue taken up in MeOH and chromatographed. The chromatogram, sprayed with Tollens reagent, showed the presence of dimeric formalbutyraldol (VII). VII was also obtained by refluxing 2 hrs. 7.2 g. iso-PrCHO, 12 g. II.HCl, and 12 ml. formalin.
 ACCESSION NUMBER: 1960:67833 CAPLUS
 DOCUMENT NUMBER: 54:67833
 ORIGINAL REFERENCE NO.: 54:12987g-1,12988a-i
 TITLE: Aldol reactions of formaldehyde and its reversibility. Comparative studies of the mechanism of the Tollens reaction, the Mannich reaction, and the acid-catalyzed aldol reaction of formaldehyde
 AUTHOR(S): Olsen, Sigurd; Henriksen, Arne; Brauer, Roar
 CORPORATE SOURCE: Univ. Blindern-Oslo, Norway
 SOURCE: Ann. (1959), 628, 1-36
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 38 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Reaction of 2,6-dimethyl-p-cresol (I) with aromatic primary amines resulted in the formation of 5,2,3-Me (HO) (HOC₂H₂)C₆H₂NH⁺CGH₄R (II). Nitroso compds. (III) were obtained upon nitrosation of II, indicating that II were secondary amines. 3-Arylbenzoxazines (IV) were prepared by reaction of II with HCHO. In the same manner N-(4-hydroxyphenyl)arylamines (V) and their nitroso compds. (VI) were obtained from 4-methylphenol (VII). Twenty-six new compds., and 2 compds. obtained by 2 new methods were prepared and studied. I and VII were synthesized by known methods, m. 129.0° and 120.0°, resp. II were prepared by the following general method. I (33.6 g.), 24.6 g. p-anisidine, and 30 ml. alc. containing 1.2 g. KOH refluxed 8 hrs., the mixture cooled, neutralized with AcOH, unreacted p-anisidine removed by steam distillation, and the resulting solid dissolved in C₆H₆, and allowed to stand 1 day gave a white solid, and crystallization gave 6.3 g. II (R = H and R = p-MeO). This compound (2.5 g.) in dilute HCl treated below 5° with 0.6 g. NaNO₂, a reddish resinous product was obtained, this dissolved in Et₂O, neutralized with dilute Na₂CO₃, washed with H₂O, and evaporation at room temperature gave a light reddish-brown crystalline solid, as the corresponding III. The following I and III were obtained (group on phenyl radical attached to the N of II, reaction time in hrs., % yield, m.p., solvent of crystallization, group in III, reaction time for III, % yield, m.p., and solvent of crystallization given): p-MeO, 8, 11.6, 120°, C₆H₅-ligroine, p-MeO, 2, 36.2, 93° MeOH; p-Cl, 10, 10.1, 106°, ethylene dichloride/ligroine, p-Cl, 3, 30.0, 131° MeOH; p-Me, 8, 8.2, 119°, p-Me, 3, 27, 101°, MeOH; p-Br, 9, 23.0, 109.5°, C₂H₄Cl₂/C₆H₆, p-Br, 4, 9.2, 135, MeOH; H, 2, 0.92, 83°, ligroine, H, 3, 29.7, 73°, MeOH-H₂O; o-MeO, 16.4, 109°, alc.-H₂O, -, -, p-EtO, 8, 10.4, 115.9°, alc., p-EtO, 24, 59, 101.3°, alc.-H₂O. II (R = p-MeO, R = H) (3 g.) in 50 ml. MeOH refluxed 2 hrs. with 1.6 ml. 37% HCHO, H₂O added, the solution cooled to room temperature, the solid collected, and recrystd. gave 3,4-dihydro-3-p-anisyl-6-methyl-8-methylol-1,3,2H-benzoxazine (IV, aryl = 3-p-anisyl). The following IV were obtained (3-aryl, reaction time in hrs., % yield, m.p., and solvent of crystallization given): p-MeOC₆H₄, 2, 32, 108°, MeOH; p-ClC₆H₄, 2, 35, 107°, Me₂CO-H₂O; p-MeC₆H₄, 2, 31.8, 83°, MeOH-H₂O; p-BrC₆H₄, 2, 48.2, 108.5°, MeOH; p-ETOC₆H₄, 0.5, 96.5, 94.3°, C₆H₅-ligroine. V were prepared in essentially the same way as were II except that 0.1 mole VII and 0.1 mole of aromatic primary amine were used. The following V (p-HOC₆H₄CH₂NHC₆H₄R-p) were thus obtained (R, time in hrs., % yield, m.p., and solvent for recrystn. given): Br, 10, 19, 86.4°, ligroine-C₆H₆; Cl, 10, 18.0, 70.5°, ligroine-C₆H₆; Me, 10, 21, 90°, ligroine-C₆H₆, 3:1; MeO, 10, 57, 111.1°, ligroine-C₆H₆, 4:1; EtO, 8, 16.0, 97.4°, ligroine-C₆H₆, 3:1. VI were prepared in essentially the same manner, except that 3.5 g. of V was used. The following VI (p-HOC₆H₄CH₂NH(CO)C₆H₄R-p) were obtained (R, time in hrs., % yield, m.p., and solvent of crystallization given): p-Br, 5, 77, 131.4°, 1:1 C₆H₆-ligroine; p-Cl, 4, 81, 118.6°, 1:2 ligroine-C₆H₆; p-Me, 3, 59, 110.6°, 2:1 ligroine-C₆H₆; p-MeO, 4, 88, 118.8°, 4:1 ligroine-C₆H₆; p-EtO, 12, 53, 98.8°, 2:1 ligroine-C₆H₆.
 ACCESSION NUMBER: 1959:121656 CAPLUS
 DOCUMENT NUMBER: 53:121656
 ORIGINAL REFERENCE NO.: 53:21734f-1,21735a-d

L19 ANSWER 39 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Condensation of CF₃ with piperidine, morpholine, and iso-Bu₂NH hydroxyacetyl deriva. produced the hydrates of CF₃CH(OH)CH₂(CH₂NR)₂ where NR = C₅H₁₀N (I), OC₄H₈N (II), and iso-Bu₂N (III). CF₃CH(OH)CH₂CH₂NCSH₁₀ (IV) was prepared by NaBH₄ reduction of CF₃COCH₂CH₂CONCSH₁₀ (V) to CF₃CH(OH)CH₂CONCSH₁₀ (VI) followed by LiAlH₄ reduction. Condensation of piperidine and HCHO with EtOCOCF₃, BuCOCF₃, and V gave the expected Mannich bases, CF₃COCH₂CH₂CH₂CONCSH₁₀-H₂O (VII). Piperidine (8.5 g.) in 17 ml. H₂O and 8.5 ml. cold 37% aqueous HCHO kept 1 hr. at 0°, the mixture treated (Cellulose-Dry Ice bath) with 11 g. CF₃, the reaction flask fitted with a Dry Ice reflux condenser, the mixture brought to room temperature in 30 min., and the precipitate recrystd. (Me₂CO) yielded 481 I, m. 93-5°, containing 2 active H atoms/mole and giving an ester by the Schotten-Baumann procedure. II, m. 83.5-7.0° (Me₂COEt), and III, m. 79-81° (Me₂CO), were similarly prepared in 36 and 20% yields. CF₃COCH₂CO₂Et (184 g.) in 200 ml. boiling dry xylene treated dropwise in an apparatus according to Kibler and Weissberger [Organic Syntheses, Collective Volume III, 109 (1955)] with 76.5 g. dry C₅H₁₀NH, the mixture refluxed 30 min., concentrated in vacuo, and fractionated gave 147 g. oily V, b₇ 119-20°, n_D²⁰ 1.4647, m. 27.4-30.0° (corrected) (petr. ether); 2,4-dinitrophenylhydrazones m. 114.5-15.5° (corrected) (dilute MeOH); Cu chelate m. 207.0-7.5° (corrected) (dilute MeOH). V (44.6 g.) in 200 ml. Et₂O stirred at 0° with portionwise addition of 4 g. NaBH₄, the mixture stirred 1.5 hrs. at room temperature, the filtered solution stirred 1.5 hrs. at room temperature with 20 ml. 5% HCl, the filtered organic layer washed, dried, and concentrated yielded 794 VI, m. 109.4-9.8° (corrected) (C₆H₆-petr. ether). VI (31.5 g.) in 100 ml. dry tetrahydrofuran and 8.7 g. LiAlH₄ in 200 ml. Et₂O processed according to Micovi. act. c and Mihailovi. act. c (C.A. 48, 10020g) and the product fractionated gave 19 g. known CF₃CH(OH)CH₂CO₂Et (VIII), b₄ 4.5 80-3°, n_D²⁵ 1.3732; phenylurethan, m. 67-9°. VIII (49.5 g.) in 75 ml. dry xylene refluxed 2 hrs. with 27 g. dry C₅H₁₀NH, the decolorized (Nuchar) solution concentrated in vacuo, the residue extracted with water and the insol. fraction recrystd. (C₆H₆) to yield 3.6 g. VI, the aqueous extract washed with C₆H₆, evaporated in vacuo, and dried by azeotropic distillation with C₆H₆ gave 12 g. piperidinium 8-hydroxy-7,7,7-trifluorobutyrate, m. 100.8-1.8° (corrected) (C₆H₆), also produced by treating CF₃CH(OH)CH₂CO₂H with C₅H₁₀NH. Unlike V, N-(acetoacetyl)piperidine (IX) was reduced successfully to 4-piperidino-2-butanol (X) with LiAlH₄. AcCH₂CO₂H (65 g.) in 70 ml. xylene at 145° treated portionwise with 34 g. C₅H₁₀NH, the mixture heated 45 min., and fractionated gave 55 g. IX, b₄ 126-8°. IX (59 g.) in 50 ml. dry Et₂O was reduced (N atmospheric) with 25 g. LiAlH₄ in 500 ml.
 ACCESSION NUMBER: 1959:51161 CAPLUS
 DOCUMENT NUMBER: 53:51161
 ORIGINAL REFERENCE NO.: 53:92251,9226a-1,9227a
 TITLE: Condensation of some trifluoromethyl ketones with secondary amines and formaldehyde
 AUTHOR(S): Grillo, G. F.; Aftergut, Siegfried; Marmor, Solomon; Carrock, Fred
 CORPORATE SOURCE: Univ. of Syracuse, Syracuse, NY
 SOURCE: Journal of Organic Chemistry (1958), 23, 366-9
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 38 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 TITLE: Synthetic products from methylolphenols, formaldehyde, and primary aromatic amines
 AUTHOR(S): Noda, Miyoshi; Shimaoka, Hiroshi; Nagase, Susumu
 CORPORATE SOURCE: Matsushita Elec. Works, Ltd., Osaka Prefecture
 SOURCE: Journal of Organic Chemistry (1959), 24, 512-15
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 dry Et₂O according to the method of Uffner and Schlittler (C.A. 43, 121g) to give 25 g. X, b₄ 103°, HCl salt m. 145° (alc.-Me₂CO); benzoate-HCl m. 192° (Me₂CO). EtOCOCF₃ (12.6 g.) treated at 0° with 8.5 g. C₅H₁₀NH and 10 ml. 37% aq. HCHO, the mixt. dild. with water, and chilled yielded 874 VII (R = Me) (XI), m. 98-100° (dil. alc.); picrate m. 105-7° (dil. MeOH). Similarly were prepd. VII (R = C₃H₇) (XII), m. 82-4° (picrate, m. 93-5°), and VII (R = CONCSH₁₀) (XIII), m. 96-8° (picrate, m. 92-3°), in 85 and 90% yields. An attempt to recrystallize XIII from hot dil. MeOH caused its decomp. to N-(6-trifluoroacetylacetyl)piperidine hydrate (XIV). V (5 g.) in 15 ml. MeOH contg. 10 drops of 15% NaOH treated dropwise at 20° with 3 g. 30% HCHO with vigorous shaking, the mixt. shaken vigorously 5 min. at 50°, treated with 5 ml. H₂O, and cooled gave 4 g. XIV, m. 138.4-40.0° (dil. MeOH). XI (5 g.) in 100 ml. Et₂O treated portionwise with 0.38 g. NaBH₄, the mixt. stirred 1.5 hrs., the filtered soln. stirred vigorously 1 hr. with 2 g. NaOH in 50 ml. H₂O, the aq. layer extd. with Et₂O, and the combined dried (MgSO₄) Et₂O solns. distd. yielded 50% 1,1,1-trifluoro-3-piperidinomethyl-2-butanol, b₄ 79-81°, p-nitrobenzoate HCl salt m. 206-8° (cor.) (CHCl₃-Et₂O). Similarly, 10 g. XII was reduced to 47% 1,1,1-trifluoro-3-piperidinomethyl-2-hexanol (XV), b₄ 92-5°, p-aminobenzoate HCl salt (XVI) m. 223-5°. Repeated attempts to purify the p-nitrobenzoate HCl salt (XVII) of XV by recrystn. from alc. failed. XVII (7 g.) in 100 ml. alc. hydrogenated with 150 mg. prerduced PtO₂, the filtered soln. evapd., the residue neutralized with NaOH, and the brown soln. dild. with H₂O yielded 63% XV p-aminobenzoate, m. 92-4°.

ACCESSION NUMBER: 1959:51161 CAPLUS
 DOCUMENT NUMBER: 53:51161
 ORIGINAL REFERENCE NO.: 53:92251,9226a-1,9227a
 TITLE: Condensation of some trifluoromethyl ketones with secondary amines and formaldehyde
 AUTHOR(S): Grillo, G. F.; Aftergut, Siegfried; Marmor, Solomon; Carrock, Fred
 CORPORATE SOURCE: Univ. of Syracuse, Syracuse, NY
 SOURCE: Journal of Organic Chemistry (1958), 23, 366-9
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 AB cf. C.A. 51, 2791b. The initial step in condensation of >CHCH:CH- with HCHO is assumed to be an electrophilic attack of HOCH₂OH₂⁺ at the terminal C atom to give >CHCH(OH)CH(CH₂OH)-. At higher acid concns. with excess HCHO dehydration may take place with formation of >C(R)CH(CH₂OH)-. Theoretically these procedures may continue until all H atoms at the terminal C atoms are substituted by CH₂OH groups and a-dioxane or tetrahydropyran rings may form from pairs of HO groups under the influence of acid. In addition the original condensation may be reversed by cleavage (cf. Zimmerman and English, C.A. 48, 11321c). These postulated reactions were studied by condensation of HCHO with PhMeC:CH₂ (I) and PhCH:CH₂ (II). HCHO (514 g., 35%), 120 g. H₂SO₄ and 180 g. (HCHO)n at 90° stirred 1 hr. with addition of 236 g. I and the mixture stirred 2 hrs. at 90°, diluted with C₆H₆ and the solution washed to neutrality, the dried solution evaporated, and the product (466 g.) distilled quickly at 3 mm., the main fractions (322 g.) fractionated at 3 mm. and the product recrystd. gave 24 g. 4-methyl-4-phenyl-m-dioxane (III), m. 39° (petr. ether) (C.A. 45, 9502d), 61 g. compound, C₁₃H₁₆O₃ (IV), m. 125.3-5.7° (alc.), and a compound, C₁₄H₁₈O₄ (V), m. 87.5-7.7°. The mother liquors and intermediate fractions (195.5 g.) treated with the calculated amount of H₃BO₃ gave 121 g. nonalc. components (VI) and 72.5 g. boric ester, hydrolyzed by stirring with 10% aqueous Na₂CO₃ on a steam bath, working up and fractionating to give 61 g. practically pure alc. component, C₁₂H₁₆O₃ (VII), converted to the 3,5-dinitrobenzoate, m. 120.0-1.0°, and recovered by 1 hr. hydrolysis of 13.0 g. salt with 13 g. Na₂CO₃ in 800 ml. 1:3 H₂O-alc. to yield 6.74 g. VII, b2.5 155°, n_D20 1.5417, d₂₀ 1.1676. VI fractionated at 0.1 mm. through a 16-plate Vigreux column with 1:10 reflux ratio yielded 12 g. III, 3 g. IV, and 16 g. V. The same reaction was carried out at lower acid concentration and a smaller excess of HCHO. I (472 g.), 684 g. 35% HCHO, 80 g. (HCHO)n stirred with 160 g. H₂SO₄ at 90° (external cooling) and stirring continued 3.5 hrs. at 90°, the product worked up and distilled to give 11 g. crude I, 230 g. high-boiling and undistillable material, the group of fractions, b. 99-115°, repeatedly crystallized (alc. and petr. ether) and the mother liquor worked up altogether 53.9 g. pure compound, C₁₁H₁₂O₂ (VIII), m. 62.0-2.5°. The remaining fractions separated by fractionation, H₃BO₃ separation and recrystn. gave 72 g. III, 52 g. IV, 1 g. V, and 67 g. VII. VIII (11.2 g.) in 35 ml. alc. hydrogenated 10 hrs. at 20° with 100 mg. PtO₂ and the filter solution evaporated gave a nearly quant. yield of 4-phenyltetrahydropyran, m. 46.0-7.0°. VIII, λ_{max} 245 mμ (log ε 4.142), is accordingly the known 4-phenyl-5,6-dihydro-1,2-pyran (cf. Borsche and Thiele, C.A. 18, 689) formed by a secondary reaction with HCHO via the intermediate H₂C:CPHCH₂CH₂OH followed by cyclization and dehydration, a reaction similar to piperidine ring formation from I observed by Schindler and Mansfield (C.A. 50, 13029f). VIII (11 g.) and 52 g. 35% HCHO stirred 4 hrs. at 90° with 12 g. H₂SO₄ and the product distilled in vacuo yielded 468 IV, m. 121-3° (alc.). IV (22 g.) and 10.2 g. Na in 100 ml. PhMe refluxed 2.5 hrs. with 29 g. (Me₂CHCH₂)₂CHOH according to Beets (C.A. 45, 9502d) and the mixture treated with 5 g. carbinol, refluxed 1.5 hrs. and treated with another 5 g., the mixture worked up and the solvents evaporated, the product treated with 20.66 g. BzCl in 23 g. C₅H₅ and the crude benzoate fractionated from alc. gave 0.61 g. IV, 15.4 g. benzoate (IX), m. 99.5-9.9°, and 1.3 g. benzoate, m. 87.4-8.1°. Treatment of the hydrogenolysis product (X) with 3,5-(O₂N)₂C₆H₃COCl gave the dinitrobenzoate (XI), m. 108.7-9.3°

L19 ANSWER 41 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB Aliphatic and cycloaliphatic aldehydes and ketones are prepared by dehydrogenating the corresponding primary or secondary dic. in the gaseous state at 350-500° in the presence of an alloy consisting of 65-75% Cu, 25-35% Zn, and a total of 0.1-1% Fe and/or Al and/or Bi. Thus, 200 g./hr. 98% BuOH is passed, by means of a measured delivery device into an evaporator heated at 200° and then enters a 1 l. brass contact chamber electrically heated to 400° containing 200 g. loosely rolled brass wire gauze (Cu 67.9, Zn 32, Fe 0.1%, and Al traces). The PrCHO formed by dehydrogenation enters a film evaporator heated to 100° and then a distillation column (provided with a cooling device) into a condensation chamber, while the H (45 l./hr.) is washed with water and enters a gasometer. The products boiling above 100° accumulated in the sump of the film evaporator (BuOH and PrCO₂Bu) reenter the evaporator through a siphon, thus returning to the cycle. A yield of 189 g. (98.5%)/hr. product containing 98% PrCHO, and 0.2% MeCH:CHCHO is obtained. With this apparatus can be produced RCHO, where R = Et, Pr, iso-Pr, iso-Bu, n-C₅H₁₁, n-C₆H₁₃, and n-C₇H₁₅ from the corresponding RCH₂OH; Me₂CO from iso-PrOH; and cyclohexanone from cyclohexanol.

ACCESSION NUMBER: 1956:82186 CAPLUS
 DOCUMENT NUMBER: 50:82186
 ORIGINAL REFERENCE NO.: 50:155761,15577a-c
 TITLE: Aliphatic and cycloaliphatic aldehydes and ketones
 PATENT ASSIGNEE(S): Farberke Hoechst AG vorm. Meister Lucius & Bruning
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 739263		19551026	GB	

L19 ANSWER 40 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 (alc.), sapon. to yield 98.7% mixt. of stereoisomeric alcs. (XII), also obtained by sapon. of IX. Formation from VIII and the characteristic spectrum, λ_{max} 260, λ_{min} 235 mμ (log ε 2.250, 1.513), showed IV to be 8a-phenyl-1,3,6-trioxadecahydronaphthalene, as confirmed by hydrogenolysis to 3-hydroxymethyl-4-phenyltetrahydropyran XII. The cis configuration was assigned to IV and the bi-equatorial configuration to IX and XI. VII (2.46 g.) refluxed 30 min. with 3 ml. MeOH and 3 ml. 36% HCl and the washed oily layer fractionated in vacuo gave 0.6 g. solid fraction, recrystd. (alc. and petr. ether) to give VIII, showing VII, 4-hydroxyethyl-4-phenyl-m-dioxane, to be the cyclization product of the triol PhC(CH₂CH₂OH)₃ with HCHO. V (25 g.) treated with 10.4 g. Na, 28.8 g. (Me₂CHCH₂)₂CHOH and 125 ml. PhMe as above and 28 g. carbinol added during the 10 hrs. reflux period, worked up and the product (21.85 g.) partially (3.57 g.) converted to the benzoate, m. 80.1-80.6° (alc.), the crude hydrogenolysis product (16.9 g.) treated with H₃BO₃ and the mixt. distd., the ester (10.2 g.) hydrolyzed and fractionated gave an alc., C₁₃H₁₈O₃ (XIII), b₃ 175-6°, n_D20 1.5360, XIII (2.06 g.) heated 1.5 hrs. at 95-100° with 50 ml. 8N H₂SO₄ in a stream of air gave HCHO, characterized as dimedob deriv., m. 187.0-7.5°. The reactions proved that only 1 hydrogenolizable O atom was present and that all O atoms are combined in 2 m-dioxane rings. It was concluded that V, λ_{max} 260, λ_{min} 235,285 mμ (log ε 2.216, 1.512, 0.588), is 4-(5-m-dioxanyl)-4-phenyl-m-dioxane, converted by hydrogenolysis into 3-(5-m-dioxanyl)-3-phenylpropanol XIII. IV and V are formed by 3 successive reactions with HCHO. As no ramification is present in II the initial step in HCHO condensation can be followed only by reversal of the reaction or formation of a new double bond as in >CHCH:CH₂OH-. H₂SO₄ (180 g.), 514 g. 35% HCHO, and 360 g. (HCHO)n stirred 30 min. at 90° with addn. of 312 g. II and the mixt. stirred 30 hrs. at 90°, the cooled mixt. worked up and the product fractionated at 3 mm. from 99 g. undistillable material gave 60.34 4-phenyl-m-dioxane and 73.5 g. fractions, b₃ 150-60°, n_D20 1.5250-70, sepd. (66.5 g.) with H₃BO₃ into 29 g. nonalc. unknown compds. and 36 g. ester, hydrolyzed to an alc. (XIV), benzoate, m. 91.6-2.0°, identical with the recently described (C.A. 50, 12059d) benzoate of 5-hydroxymethyl-4-phenyl-m-dioxane, demonstrating that the formation of a new double bond in the primary reaction product with HCHO is possible, although an extremely slow reaction.

ACCESSION NUMBER: 1959:23328 CAPLUS
 DOCUMENT NUMBER: 53:23328
 ORIGINAL REFERENCE NO.: 53:42801,4281a-i,4282a-c
 TITLE: Reaction of α-methylstyrene with formaldehyde
 AUTHOR(S): Beets, M. G. J.; van Eszen, H.
 SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (1957), 76, 1009-20
 CODEN: RTCPB4; ISSN: 0370-7539
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 42 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB MePhC:CH₂ (I) and β-pinene (II) condense with CH₂O and secondary amines in AcOH-H₂SO₄ according to the equation: -CHC: + CH₂O + HNR₂ → -C(CCH₂NR₂). Anethole (III) under similar conditions reacted principally with the formation of a product of the type -CHC(CH₂NR₂)COAc. H₂SO₄ (10 cc.) in 300 cc. glacial AcOH treated with cooling with 140 g. 40% aqueous Me₂NH, 34.5 g. paraformaldehyde, and 118 g. the mixture refluxed 3 hrs. under N, cooled, neutralized with 230 g. NaOH in 600 cc. H₂O, and extracted with 200 cc. Et₂O, the aqueous layer washed with two 100-cc. portions Et₂O, and the combined Et₂O solns. washed with H₂O, dried, and fractionated yielded 77 g. Me₂NCCH₂CH₂CPHCH₂, b₁₂ 110-14°, n_D25 1.5226-1.5228 (oxidized with KMnO₄ it gave BzOH); methiodide, m. 162-3° (from absolute EtOH); HCl salt, noncrystallizable oil. Similarly were prepared the following CH₂:CPHCH₂CH₂R' (R', & yield, b.p./mm., and n_D25 and m.p. of HCl salt given): Et₂N, 8.9, 82-5°/0.3, 1.5131-1.5149, 120-2°; piperidine (IV), 28.5, 115-16°/0.20-0.25, 1.5375-1.5385, 205-6° (methiodide, m. 131-3°); pyrrolidino, 6.0, 95-7°/0.4, 1.5401, 117-19°; morpholino, 32.4, 98-101°/0.2-0.3, 1.5421-1.5422, 177-9° (methiodide, m. 123-5°). I (35 g.) in 80 cc. 95% EtOH hydrogenated 2 hrs. at 60 lb. pressure over 5 g. Raney Ni and the mixture filtered and distilled gave 28.0 g. MePh(CH₂)₃NMe₂, b₁₉ 112-13°, n_D25 1.4940; HCl salt, m. 165-7°. Similarly were prepared the following compds. MePh(CH₂)₃R' (R', b.p./mm., n_D25, and m.p. of the HCl salt given): Et₂N, 68-70°/0.3, 1.4910-1.4915, 115-16°; piperidino, 109-12°/0.3, 1.5130-1.5135, 168-70°; pyrrolidino, 75-6°/0.3, 1.5132, 137-9°; morpholino, 95-6°/0.25, 1.5153, 177-9°. I (52.5 g.) added slowly to 117 g. concentrated H₂SO₄ at 5°, and the product washed and distilled gave 25 g. distillate, b₂ 190-2°, n_D25 1.5478-1.5480, apparently 1,3-bis(dimethylaminomethyl)-1-methyl-3-phenylhydridan. Cyclohexene, styrene, and Ph₂C:CH₂ subjected to the condensation with paraformaldehyde and piperidine in the presence of AcOH gave only 65, 80, and 90% yields, resp., of the unchanged starting materials. I condensed with CH₂O and a secondary amine gave the corresponding nopylamines [nopyl-2-(6,6-dimethylbicyclo[1.1.3]hept-2-en-2-yl)ethyl] (& yield, b.p./mm., and n_D25, and m.p. of HCl salt given): N-nopylpiperidine (V), 47.5, 101-2°/0.4, 1.4967-1.4970, 253-5°, n_D20 -22.3 to -24.8° (methiodide, m. 201-2°; V.Me₂SO₄, 145-8°). N-nopylpyrrolidino, 20, 82-3°/0.3, 1.4946-1.4949, 229-31°; N-nopylmorpholino, 30, 104-6°/0.3, 1.4991-1.5020, 218-20°. V in EtOH hydrogenated at 100° and 1000 lb. pressure over Pd-C yielded 55% N-dihydronopylpiperidine, b₀ 35 95-6°, 1.4929-1.4934, 277-82°; methiodide, m. 221-3°; methosulfate, m. 171-3°. Similarly was obtained N-dihydronopylpyrrolidino, 71a, 89-93°/0.3, 1.4911, 235-7°. Nopol (16.6 g.) in 80 cc. pyridine treated at 5° with 20.7 g. p-MeC₆H₄SO₂Cl, the mixture held at 5° overnight, and treated with H₂O, ice, and Et₂O, the Et₂O layer washed with dilute HCl, and H₂O, dried and evaporated, the crude residue refluxed 2 hrs. with 25 g. piperidine in 80 cc. Me₂CO, allowed to stand overnight, and diluted with 200 cc. Et₂O, and the precipitate (20.5 g.) recrystd. from EtOAc-EtOH gave piperidine p-toluenesulfonate, m. 130-2°, the Et₂O-Me₂CO filtrate treated slowly with 50 cc. concentrated HCl, and the precipitate (22.5 g.) recrystd. twice from H₂O yielded V.HCl, m. 252-5°

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(decompn.); free V, b.p. 93-5°, nD₂₅ 1.4952-1.4960, d₂₀
-18.80° (1 dm., neat). III (148 g.), 37.5 g. paraformaldehyde, and
10 cc. concd. H₂SO₄ in 400 cc. glacial AcOH refluxed 9.5 hrs., 150 cc.
AcOH distd. off at 15 mm., the residual mixt. dild. with 500 cc.
Et₂O, the soln. treated dropwise with cooling with 185 g. NaOH in 600 cc.
H₂O with stirring, the aq. layer extd. with 300 cc. Et₂O, and the combined
Et₂O layer and ext. washed, dried, and fractionated yielded 30 g.
1-(p-methoxyphenyl)-2-methyl-3-piperidino-1-propyl acetate (VII), b.p. 4
146-7°, nD₂₅ 1.5140, and m. 53-4° (from aq. EtOH). The
solid and the liquid VI gave the same HCl salt, m. 173-4°
(decompn.). Another run with III gave VI, b.p. 5 160°, nD₂₅
1.5169-1.5172. VI oxidized with alk. KMnO₄ gave p-MeOC₆H₄CO₂H, m.
182-4°. VI refluxed with KOH in aq. EtOH, the mixt. dild. with
H₂O, the ppt. oil taken into Et₂O, the soln. washed, dried, and treated
with dry HCl, and the gummy ppt. washed with EtOAc and recrystd. from
Me₂CO gave 1-(p-methoxyphenyl)-2-methyl-3-piperidino-1-propanol (VII) HCl
salt, m. 170-2°. VI.HCl allowed to stand several weeks in
Me₂CO-EtOAc gave prisms, m. 120-1°, and needles, m. 172-4°;
the 2 diastereoisomeric alc. HCl salts crystd. apparently separately. VII
(3.32 g.) and 1.24 g. Na₂Cr₂O₇ in 35 cc. AcOH heated slowly to 80°,
chilled, covered with Et₂O, and treated with 50 g. NaOH in 100 cc. H₂O,
the Et₂O layer washed, dried, and treated with dry HCl in Et₂O, and the
pptd. semisolid gum crystd. from Me₂CO-abs. EtOH gave 1-(p-methoxyphenyl)-
2-methyl-3-piperidino-1-propanone-HCl, m. 173-5° (decompn.) (sealed
tube)
ACCESSION NUMBER: 1956:27968 CAPLUS
DOCUMENT NUMBER: 50:27968
ORIGINAL REFERENCE NO.: 50:5676g-1,5677a-h
TITLE: The reaction of formaldehyde and
secondary amines with some olefins
AUTHOR(S): Hennion, G. F.; Price, Charles C.; Wolff, Vernon C.,
Jr.
CORPORATE SOURCE: Univ. of Notre Dame, Notre Dame, IN, USA
SOURCE: Journal of the American Chemical Society (1955), 77,
4633-6
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English

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g. Raney Ni in 2 cc. alc. treated in portions with 12 cc. 2N NaOH, boiled,
cooled, filtered, and acidified with dil. H₂SO₄, gave 0.25 g.
o-MeC₆H₄OCH₂CO₂H (XII), m. 149° (mixed m.p. with authentic sample,
150°). VI treated similarly also gave XII, thus establishing the
o-directed substitution in the Mannich bases. XI (4.8 g.) and 3.6 g.
CH₂ClCO₂Et added to 0.46 g. Na in 20 cc. abs. EtOH, refluxed 1 h., the
alc. evapd., and the residue treated with H₂O, extd. with Et₂O, dried,
concd., and treated with dry HCl gave 35% Et (1-morpholinomethyl-2-
naphthyl)acetate HCl salt (XIII), m. 185° (from VII). XIII and
several of the Mannich bases (no details given) were found inactive toward
plants in the "pea test" and in a test on elongation of corn roots.
ACCESSION NUMBER: 1956:27718 CAPLUS
DOCUMENT NUMBER: 50:27718
ORIGINAL REFERENCE NO.: 50:5547c-1,5548a-b
TITLE: A study of the Mannich reaction between some
substituted phenols and secondary amines
AUTHOR(S): Julia, Marc; Tchernoff, Georgette
CORPORATE SOURCE: Ecole polytech., Paris
SOURCE: Bulletin de la Societe Chimique de France (1955) 830-3
CODEN: BSCFAS; ISSN: 0037-8968
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 50:27718

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AB Cresols and chlorophenols were condensed with Me₂NH (I), Et₂NH (II),
morpholine (III), or piperidine (IV). In all the products substitution
took place in the o-position to the phenolic OH, although the moderate
yields allow for the possibility that other products, not isolated, were
also formed by a different substitution mechanism. All the products from
I or III were soluble at room temperature in 5% NaOH while those from II or
IV were generally insol. The strong amine bases were sufficiently active to mask
the phenolic behavior. The products were tested and found inactive as
antimalarials. In preparation method (A), equimolar amts. of the phenol,
40% CH₂O, and I or II were allowed to stand in alc. for several hrs., refluxed
2 h., concentrated, taken up in Et₂O, extracted with 2N HCl, made basic,
extracted with
Et₂O, and the extract washed, dried, and fractionated after evaporation of
the solvent. In method (B), the phenol, CH₂O, and III or IV in alc. were
refluxed 1-2 h. with a small amount of concentrated HCl and worked up as in
(A).
The following X-substituted (2-hydroxybenzyl)dimethylamines were prepared
(X, m.p., b.p./mm., % yield, and m.p. of the picrate and HCl salt given):
3-Me, -, 78-85°/0.3, 50, -, 129°; 4-Me, 44°,
99°/0.2, 60, -, hygroscopic; 5-Me, -, 88°/1, 68,
168°, 156°; 3-Cl (VI), -, 117°/1, 30, 167°;
167°; 4-Cl (VII), -, 103°/0.5, 40, 159, hygroscopic; 5-Cl, -,
92°/0.1, 68, -, 165° [from anhydrous Et₂O-EtOH (VII)]; 3,5-Cl₂,
60° (from EtOH), -, 30, -, 185°. Prepared similarly were the
following X-substituted (here and subsequently in this abstract the X
substituent is in the benzyl group) (2-hydroxybenzyl)diethylamines: 3-Me,
-, 93-7°/0.5, 30, -, 153°; 4-Me, -, 107°/0.5, 36,
142°, 108°; 5-Me, -, 100-5°/0.1, 40, -, 152°;
3-Cl, -, 105-10°/2, -, 151° [from absolute C₆H₅EtOH (VIII)];
4-Cl, -, 120°/2, -, 162°, 123°; 5-Cl,
122°/1, 56, -, 150°; 3,5-Cl₂, -, 130-40°/0.5, -, -,
170° (from VIII); the following X-substituted 1-(2-hydroxy-
benzyl)piperidines: 3-Me, -, 110°/0.2, -, 184°, 186°;
4-Me, 55° [from aqueous EtOH (IX)], -, 21.5, 132°, 183°;
5-Me, -, 115°/0.2, -, 150°, 188°; 3-Cl, 49°
(from IX), -, 15, -, 185°; 4-Cl, -, 156°/5, 15, -,
204° (from VIII); 5-Cl, 57° (from IX), -, 18, -, 232°;
3,5-Cl₂, 80° [from petr. ether (X)], -, 192° the
following X-substituted 4-(2-hydroxybenzyl)morpholines: 3-Me, -,
120°/0.5, 15, 201°, 196° (from VII); 4-Me, 64°
(from IX), -, 21, 165°, 190° (from VII); 5-Me, 54°
(from X), -, 25, -, 204°; 3-Cl, 114° (from EtOH), -, 44.5,
201°, 197°; 4-Cl, 57° (from X), -, -, 178°;
5-Cl, 60° (from X), -, 20, 202°, 191°; 3,5-Cl₂,
89° (from IX), -, -, -, 200°. Also prepared by this method
were 90% 1-(2-hydroxy-1-naphthylmethyl)-piperidine, m. 95° (HCl
salt, m. 145°), and 89% 4-(2-hydroxy-1-naphthylmethyl)morpholine
(XI), m. 115° (from IX), (HCl salt, m. 177°). In the
structure proofs, 8 g. V and 4 g. Cu chromite in 100 cc. dioxane were
heated 5 h. at 150° in an autoclave under 130 kg. H, cooled, the
catalyst was filtered off, most of the solvent evaporated, the residue
poured
into H₂O, extracted with Et₂O, and the extract dried, freed of solvent, and
distilled, giving 2 g. of a mixture of o-cresol and 6,2-Cl₂MeC₆H₃OH.
The phenols, e.g. 5,2-Cl₂MeC₆H₃OH, were converted to the corresponding
phenoxycetic acids, e.g. 5,2-Cl₂MeC₆H₃OCH₂CO₂H, of which 0.4 g. with 1.2

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AB cf. C.A. 50, 7989. An investigation to ascertain the influence of
structural and elec. factors upon the mode of cleavage of substituted
allyl ethers by Grignard reagents indicated that aryl and alkyl (lower
than C₇H₁₅) Grignard reagents cleave substituted allyl ethers by a
1,2-mechanism, while C₇H₁₅MgBr and C₈H₁₇MgBr cleave both mono- and
disubstituted allyl ethers by a 1,4-mechanism. The condensation of the
appropriate Na alkoxide and alkyl halide gave the following allyl ethers
(b.p./mm., nD₂₀, d₂₀, and M RD given): PhCH₂CH₂OCH₂CH₂CH₂ (I),
115-16°/37, 1.5200, 1.0015, 49.14; PhCH₂CH₂OCH₂CH₂CH₂CH₂ (II),
121-3°/34 (70-4°/1), 1.5390, 1.0019, 74.40; BuOCH₂CH₂CH₂CH₂
(III), 132-4°/13, 1.5510, 0.9841, 61.73. The appropriate aldehydes
and Grignard reagents condensed and the resulting secondary alc.
converted to the Na derivs. and treated with the suitable alkyl halide
gave the following allyl ethers (same data given): BuOCH₂CH₂CH₂CH₂CH₂ Me (IV),
179-81°/748, 1.4328, -, (d₂₂ 0.8210), 58.27; Me₃COCH₂(CH₂Me)
(V), 164-5°/752 (104°/60), 1.4671, 0.8960, -. The
appropriate allyl ether (3-5 g.) in 50-75 cc. hexane treated with ozone at
0° the mixture decomposed with Zn dust, H₂O, traces of hy quinone,
and AgNO₃, and the products isolated as described previously (C.A.
49,833c) gave the corresponding aldehydic cleavage products (the 2
aldehydes formed, their b.p./mm., nD₂₀, d₂₀, and the m.p. of their
2,4-dinitrophenylhydrazones given): I, BzH, 55-6°/50, 1.4600,
0.999, 236-7° and PhCH₂CH₂OCH₂CH₂CHO, 94-5°/10, 1.5105,
1.282, 111-12°; III, BzH, 145-7°/700, 0.986, 1.4700,
238-9°, and BuOCH₂CH₂CHO, 130-2°/746, 1.4289, 0.854,
89-90°; IV, AcH, -, -, 147-9°, and Bu(BuO)CHCHO,
90-3°/29 (153-4°/756), 1.4230, 0.915, 96-7°; V, AcH,
-, -, 145-6° and Me₃COCH₂(CH₂Me)CHO, 132-3°/753, 1.4279,
0.884, 87-8°; BuOCH₂(CH₂Ph)CH₂CH₂CH₂ (VI), BzH, 164-5°/749, -,
0.925, 235-6°, and PhCH₂CH₂(OBu)CHO, 110-12°/749, 1.4180,
0.848, 99-100°. The appropriate allyl ether in Et₂O or C₆H₆ added
to the suitable Grignard reagent during 2-4 h. the mixture refluxed 20-40
h., and hydrolyzed with saturated aqueous NH₄Cl, the aqueous layer
extracted continuously
with Et₂O, the organic layer and the extract combined, dried, and
evaporated, and
the residue distilled gave the corresponding olefin and alc. I and
C₆H₁₃MgBr gave 22% 1-nonene (VII), b₇₄₈ 143-6°, nD₂₀ 1.4261, d₂₀
0.8155, and 94% PhCH₂CH₂OCH₂ (VIII), b₇₄₈ 201-3°, nD₂₀ 1.5179, d₂₀
1.0001, M RD 37.08 (3,5-dinitrobenzoate, m. 105-6°). II and
C₆H₁₃MgBr gave 15% 1-phenyl-1-nonene (IX), b₇₄₆ 140-3°, nD₂₀
1.4261, d₂₀ 0.8323, and 23% VIII. II and PhMgBr yielded 17% PhCH₂CH₂CH₂CH₂CH₂ (X),
b₁₅ 112-15°, nD₂₀ 1.5501, d₂₀ 1.0019, M RD 62.48, and 98%
VIII. II and PhCH₂MgBr gave 47% PhCH₂CH₂CH₂CH₂CH₂ (XI), b₁₃ 145-8°,
nD₂₀ 1.5639, d₂₀ 1.0172, M RD 66.58, and 83% VIII. II and PhCH₂MgBr
yielded 41% XI, b₆ 98-9°, and 25% BuOH, b₇₄₅ 112-15°
(3,5-dinitrobenzoate, m. 68-9°). III and C₈H₁₇MgBr gave 24%
3-phenyl-1-undecene (XII), b₇₅₃ 145-6°, nD₂₀ 1.5050, d₂₀ 0.876, M
RD 77.79, and 88% BuOH. IV and EtMgBr yielded 83% MeCH₂CH₂CH₂CH₂Et (XIII),
b₇₄₂ 188-9°, nD₂₀ 1.4339, d₂₀ 0.805, M RD 45.28, and 23% BuOH. IV
and BuMgBr gave 68% MeCH₂CH₂CH₂CH₂ (XIV), b₇₄₈ 180-2°, nD₂₀ 1.4440,
d₂₀ 0.8408, and 35% BuOH. V and C₈H₁₇MgBr yielded Me₃COCH₂CH₂CH₂MeC₈H₁₇
(XV), b₇₅₃ 135-8°, nD₂₀ 1.4305, d₂₀ 0.822, M RD 74.03, and 88%
Me₃COH, b₇₅₃ 83-5° (3,5-dinitrobenzoate, m. 140-1°). V and
PhMgBr gave 30% MeCH₂CH₂CH₂CH₂Me (XVI), b₇₅₂ 171-3°, nD₂₀ 1.5040,
d₂₃ 0.9880, and 30% Me₃COH. VI and C₈H₁₇MgBr yielded 59% PhCH₂CH₂CH₂CH₂CH₂CH₂ (XVII),
m. 49.5-50°, and 63% BuOH. The olefinic
reaction products were identified by ozonization. The olefins used in the
ozonization and the 2 aldehydes formed were (b.p./mm. and nD₂₀ of the

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 aldehydes and the m.p.s. of their 2,4-dinitrophenylhydrazones given): VII, CH2O, -, -, 165-6°, and C7H15CHO (XVIII), 100-1°/700, 1.4278, 106-7°; IX, BzH, 100-2°/700, -, 233°, and XVIII; X, BzH and PhCH2CHO, -, -, 120-1°; XI, BzH and Ph(CH2)2CHO, -, -, 144-5°; XII, CH2O and 2-phenylcapraldehyde, 101-2°/733, 1.4111, 122-3° (see below); XIII, AcH, -, -, 145-6°, 2-ethylcapraldehyde, -, -, 119-20°; XIV, AcH, and 2-phenylcapraldehyde, 120-1°/742, 1.3979, 107-8° (d20 0.879); XV, Me3CCHO, 81-2°/744, 1.3709, (d23 0.817), 103-4°, and 2-methyldecanal, 119-20°/744, 1.4205 (d23 0.8948), 63-4°; XVI, AcH and 2-phenyl-3,3-dimethylbutanal, 115-18°/744, -, 70-1°; XVII, PhCH2CHO, 179-81°/748, -, 121-2° and 2-phenylcapraldehyde, -, -, 85-6° (sic).
 ACCESSION NUMBER: 1956:23948 CAPLUS
 DOCUMENT NUMBER: 50:23948
 ORIGINAL REFERENCE NO.: 50:4835a-1.4836a-b
 TITLE: Grignard reagents and unsaturated ethers. V. Mode of cleavage of α - and γ -substituted allyl ethers by Grignard reagents
 AUTHOR(S): Hill, Carl M.; Simmons, Doris E.; Hill, Mary E.
 CORPORATE SOURCE: Tennessee A. & I. State Univ., Nashville
 SOURCE: Journal of the American Chemical Society (1955), 77, 3889-92
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 AB A primary or secondary alicyclic amine with HCHO and HCO2H produces an alicyclic tertiary amine, RMeR' where R is a cycloalkyl group and R' is an alkyl or cycloalkyl group. To 119.5 parts 85% HCO2H at 5° was added 99.2 parts cyclohexylamine, then 179 parts 37% HCHO, with the temperature kept at 5-10°, and the mixture stirred and heated to 56° until CO2 was evolved, whereupon heating was discontinued; the temperature rose about 26°. When the exothermic reaction was over, the mixture was heated 3.5-4 hrs. at 90-5°, cooled to 50°, 126 parts concentrated HCl added, and the excess HCHO and HCO2H removed by distillation, the vapor temperature reaching 108°. To the residue was added 242 parts 25% NaOH, and the resulting upper layer distilled to give 2 fractions (I and II). I, b. 95-6°, contained 2 layers: the organic layer was dried and added to II which b. 158-9° and was N,N-dimethylcyclohexylamine (yield, 80-3%).
 ACCESSION NUMBER: 1955:73637 CAPLUS
 DOCUMENT NUMBER: 49:73637
 ORIGINAL REFERENCE NO.: 49:14027d-f
 TITLE: Tertiary alicyclic amines
 PATENT ASSIGNEE(S): Monsanto Chemical Co.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 716649		19541013	GB	

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 AB The condensation of CH2O and secondary amines with thiophenols yielded aryl dialkylaminomethyl sulfides (I) and not the expected Mannich bases. The picrates of the I are described, p-O2NC6H4COCl formed stable compds., presumed to be sulfonium salts, with the I obtained from p-MeC6H4SH and the thionaphthols, whereas from the other I only the p-nitrobenzoate of the original thiophenol could be isolated. 2,5-Br2C6H4SO2Cl reduced with Zn yielded 50% 2,5-Br2C6H3SH, m. 39-40°. The appropriate secondary amine added dropwise to an equimolar amount of the thiophenol below 20° (in most cases a precipitate of the addition product appeared), the mixture treated with an equivalent amount
 37% aqueous CH2O, heated during 1 h. up to 80°, kept 2 h. at 80°, and cooled, and the solid deposit recrystd. from EtOH or ligroine gave the desired I; if the crude product was an oil, the oil was extracted into Et2O, the solution dried with MgSO4 and evaporated at 20 mm. pressure
 and about 50°, and the residue distilled in vacuo. In this manner were prepared the following aryl piperidinomethyl sulfides (aryl group, m.p. or b.p./mm., % yield, and m.p. of picrate given): Ph, 138-41°/5-6, (n25D 1.5789, d30 1.0520), 67, 142-3°; o-MeC6H4, 133-5°/2-3, 45, 149-51°; m-MeC6H4, 141-2°/2-3, 64, 133-4°; 2-ClOH7 (II), 48-9°, 89, -; 1-ClOH7, (III), 136-7°, 89, -; p-O2NC6H4, 90-3° (from ligroine), 59, -; p-ClC6H4, 47-9°, 43, 160-1°; p-BrC6H4, 54-5°, 44, 162-3°; 2,5-Br2C6H3, 39-40°, 47, 157-8°; p-MeOC6H4, 127-31°/4-5, 38, 145-6°; p-MeC6H4 (IV), 32-2.5°, -76, -; 2,4,6-Me3C6H2, 46-7°, 22, 179-81°; the following aryl morpholinomethyl sulfides (same data given): Ph, 146-9°/5-6, (n25D 1.5809, d30 1.1251), 33, 132-3°; o-MeC6H4, 138-40°/2-3, 54, 159-60°; m-MeC6H4, 133-7°/2-3, 79, 145-7°; 2-ClOH7 (V), 47-8°, 96, -; 1-ClOH7 (VI), 73-4°, 88, -; p-O2NC6H4, 79-81° (from ligroine), 70, -; p-ClC6H4, 60-1° 79, 172-3°; p-BrC6H4, 66-6.5°, 69, 172-4°; 2,5-Br2C6H3, 84-5°, 61, 174-5°; p-MeOC6H4, 50-1°, 73, 158-9°; p-MeC6H4 (VII), 38-8.5°, 96, -; 2,4,6-Me3C6H2, 60-2°, 26, 174-5°; and the following aryl diethylaminomethyl sulfides (same data given): Ph, 110-12°/5-6, (n25D 1.5500, d30 0.9878), 71, 87.5-89°; o-MeC6H4, 115-17°/2-3, 67, 108-10°; m-MeC6H4, 114-17°/2-3, 55, 87-9°; p-ClC6H4, 135-8°/2-3, 43, 124-5°; p-BrC6H4, 110-15°/2-3, 38, 127-8°; 2,5-Br2C6H3, 122-4°/4-5, 31, 112-13°; p-MeOC6H4, 107-10°/4-5, 40, 110-11°; p-MeC6H4, 113-14°/2-3, (n20D 1.5481, d30 0.9804), 58, -; 2,4,6-Me3C6H2, 138-40°/3-4, 40, 149-50°; all compds. were recrystd. from EtOH except where stated otherwise. The appropriate I (15 g.) in 100 cc. dry PhMe was treated with 11 g. p-O2NC6H4COCl in 50 cc. dry PhMe, the mixture refluxed 2 h., and the resulting addition product, presumed to be a sulfonium salt, recrystd. from 95% EtOH. In this manner were prepared the p-O2NC6H4COCl-I addition products (m.p. given) from the following I: IV, (adduct = C20H23ClN2O3S), 108-9°; VII, 155-5.5°; VIII, 193-4°; II, 159-60°, V, 176-8° (all from EtOH); III, 198-200° (from 1:1 dioxane-EtOH by adding H2O); VI, 180-2° (from 6:4 dioxane-EtOH). The following I (aryl group given) gave under the same conditions only the p-nitrobenzoates of the corresponding thiophenols (m.p. and % yield given): p-ClC6H4, 144-5°, 57; p-BrC6H4, 179-9.5°, 54; 2,5-Br2C6H3, 146-7°, 49; p-O2NC6H4, 150-3°, -; p-MeOC6H4, 120-1°, 63; 2,4,6-Me3C6H2 (IX), 94-6°, 55; all esters were recrystd. from 95% EtOH. The

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 p-nitrobenzoates did not sep. from the cooled PhMe solns.; the solns. were, therefore, concd. to beginning crystn. The esters were also synthesized independently from the chloride and the thiophenols in 50-60% yields. IX was prepd. by dissolving the thiophenol in 10% aq. NaOH, adding a slight excess of p-O2NC6H4COCl, shaking the mixt. 2 h., and recrystg. the yellow solid product from 95% EtOH.
 ACCESSION NUMBER: 1955:53525 CAPLUS
 DOCUMENT NUMBER: 49:53525
 ORIGINAL REFERENCE NO.: 49:10279g-1.10280a-f
 TITLE: The condensation of thiophenols with secondary amines and formaldehyde
 AUTHOR(S): Grillet, Gerald F.; Felton, Herman R.; Garrett, Beverley R.; Greenberg, Harold; Green, Richard; Clementi, Robert; Moskowitz, Mark
 CORPORATE SOURCE: Syracuse Univ., Syracuse, NY
 SOURCE: Journal of the American Chemical Society (1954), 76, 3969-71
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 49:53525

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 AB cf. C.A. 46, 3844c. Different methods for preparing pure solns. of HCHO (I) are discussed, and the best conditions necessary for obtaining solns. of a high degree of purity are described. The conditions under which polyoxymethylene (II) of various degrees of polymerization (d.p.) can be prepared are then described. Finally the reactions which take place when polyoxymethylenes are dissolved in water in the absence and in the presence of acids and bases are indicated, and the existence of maximum points on the concentration-time curves of products of low d.p. is explained. In purifying I by distillation of com. I containing MeOH, not all MeOH can be eliminated under any conditions, and, contrary to Natta and Baccaredda (C.A. 27, 4996), e.g., aqueous I containing 5-6% MeOH, distilled to 0.25 volume, gives a residue containing 0.5% MeOH. This is the min. obtainable because of continuous formation of MeOH and HCO₂H (III), irrespective of the pH. If the solution is buffered by CaCO₃ or MgCO₃, much more MeOH is formed. When 0.5% MeOH is unobjectionable, the method is rapid and efficient with a tall fractionating column. The distillation residue is neutralized, 0.4% NaOH added, the mixture allowed to stand 2 days, filtered, and the precipitate washed with water, and dried over P₂O₅, yielding an amount of pure II corresponding to approx. 0.5% of the I. II is difficult to dissolve in water, e.g., to prepare a 25% solution it must be refluxed 4 days, and then the solution contains 0.4% III. But II in 0.1N H₂SO₄ refluxed 3-4 hrs., or a suspension of II in 0.1N NaOH agitated 10 min., brought to pH 2-3 with H₂SO₄, and filtered, gives a 15% solution of I, which, when distilled, yields solns. of I having pH 3-3.5 and containing only 0.05% III. In the preparation of II from concentrated aqueous I (cf. C.A. 46, 8494h), various d.p. values can be obtained at room temperature thus: 15-fold from 40% I at pH 7 in 4-6 hrs.; 30-35-fold under the same conditions in 50-70 hrs., and 80 to 100-fold from 35% I at pH 9-10 in 30-40 days. The solubilization of II was studied, not under the restricted conditions of Lobering (C.A. 30, 7978.1) or Sauterey (C.A. 46, 7854i), but at 20° with wide ranges of concentration in 0.1N NaOH and of time, and with highly purified II of various d.p. values. When the concentration of I is plotted against time, maximum concns. of I are evident for all polymers (the higher the d.p. the lower this maximum), and all concns. decrease asymptotically to the same ultimate concentration (18%) with time. Evidence shows that this decrease is not attributable to the formation of II and III nor to other reactions, such as aldol condensation. I solns. are of 3 types. (1) Unstable solns., i.e., of concns. above the stability limit (s.l.), from which II of 7-10 d.p. seps. (2). Below this concentration, metastable solns. with supersat. only of II of higher mol. weight, exist and these represent the true equilibrium concentration (e.c.) of the heterogeneous solid II-aqueous I system. (3) Stable solns., of concns. below the e.c., not saturated with II. Preliminary expts. indicate that the dissociation tension (d.t.) of the equilibrium, HO(CH₂O)_nH . dblwr. HO(CH₂)_n-1H + I, decreases with increase of the mol. weight of II. II with low d.p. in contact with metastable solns. undergo an "aging" process, with resulting increase of mol. weight, because their d.t. is less than the partial pressure

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 AB Three principal factors control β-hydroxy carbonyl formation (aldol and ketol condensation): (1) enolization with a basic or acidic catalyst; (2) induced cationoid character of alternate C atoms in a chain; and (3) steric effects. The cationoid effect is especially pronounced in aldehydes. Mixed aldehyde-ketone condensations are facilitated by the fact that the α-C of the ketone is a strong electron donor and the carbonyl C of the aldehyde is a strong electron acceptor. The principal reaction product of RCHO with R'CH₂COCH₂R'' is RCH(OH)CH(R')COCH₂R''. Three types of mixed ketolization are distinguished: (1) vinyl ketone and aldehyde with high concentration of soda (10N aqueous), (2) Powell type, with cautious introduction of aldehyde, low catalyst concentration, in alc., and (3) Grignard-Dubien type, aqueous and ethereal, with high catalyst concentration and cautious and progressive introduction of aldehyde. Powell type ketolizations were performed by maintaining the ketone at constant temperature in a Mariotte flask with shaking, adding the catalyst as alc. KOH, introducing AcH slowly as vapor, neutralizing with (CO₂H)₂, and distilling. The yield of AcCH₂CH(OH)Me (I) from AcH and Me₂CO decreased from 55% at 15° to 0% at 70° (5:1 Me₂CO-AcH molar ratio and about 0.7% KOH), increased from 35.7% to 84% with an increase in Me₂CO-AcH molar ratio to 2.25:13.2 (at 12.5-15° with 1% KOH) and decreased linearly from 84% to 46% with an increase in KOH concentration from 0.37 to 2.8% (5:1 Me₂CO-AcH). Condensation of CH₂O with ketones was difficult because of resinification but fair yields of ketols were obtained with the aid of anhydrous CH₂O. AcEt (144 g.), 30 g. 30% CH₂O in EtOH, and 3 g. K₂CO₃ agitated 12 hrs. at 22° gave 38 g. AcCHMeCH₂OH (II). AcPr and CH₂O similarly gave 45% AcCHEtCH₂OH (III), n_D 1.4377, d₁₅ 1.511.5 0.979, b₁₆ 96-103°. II (20 g.) and 4 g. ZnCl₂ on distillation gave 10 g. AcCHMeCH₂ b. 76°. III similarly gave AcCHEtCH₂ (IV), b. 114-117°. Hydrogenation of IV in the presence of Raney Ni-Pt gave AcCHMeMe, b₁₇ 114-117°; semicarbazone, m. 94-5°. AcCHMe₂ and CH₂O as in preparation of II gave 40% AcCHMe₂CH₂OH, b₁₅ 85°. AcCHMe₃ and CH₂O did not give an identifiable ketol. AcAm and CH₂O gave 42% AcCHBuCH₂OH (V), b₁₂ 112-14°, d₁₄ 1.042, n_D 1.438. V and ZnCl₂ gave the corresponding vinyl ketone which on hydrogenation gave AcCHMeBu, b. 162°; semicarbazone, m. 80°. AcCHMe₃ and CH₂O gave 46% AcCHAMeCH₂OH, b₁₄ 128°, d₁₃ 1.033, n_D 1.442. iso-PrCHO (144 g.), 50 g. Me₂CO, and 70 ml. N Me₂CO stirred 7 hrs., neutralized with (CO₂H)₂, and vacuum distilled gave 38 g. iso-PrCH(OH)CH₂Ac, b₁₃ 85-7°. Chemical properties of two secondary β-ketols, I and MeCOCHMeCH(OH)Me (VI), were studied in detail. Thermal stability of the pure ketols is good: I can be distilled at atmospheric pressure and VI yellows only slightly after 36 hrs. at 95°. In even feebly alkaline medium they slowly decompose into the original ketone and aldehyde. Distn from acidic medium and treatment with AcCl cause dehydration to vinyl ketones VI (50), 50 g. Ac₂O, and 1 drop C₅H₅N distilled, the distillate (b₁₃ 89-91°) washed with H₂O, dried, and redistd. gave 35 g. VI acetate, b₁₂ 88-92°, d₂₆ 1.080. Reaction with dinitrophenylhydrazine gave the following hydrazones (ketone and m.p. given): AcCHMeCHMe, 155°; AcCHMeCHMe, 194°; AcCHMeCHMe, 161°. p-IC₆H₄CONHNH₂ gave the following derivs. (ketone and m.p. given): I, 133-4°; VI, 150°; II, 84-5°. The p-carboxyphenylhydrazone of II formed similarly.

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 of the I in soln. These facts make possible an easy interpretation of the phenomena when solid II is in contact with water (neutral, acidic, or alk.). The higher the temp., the higher the e.c. and s.l. The expts. were performed at 20°, and at this temp. the e.c. is approx. 18% and the s.l. concn. 35%. The mean d.p. of the II as ppt. is around 50, and that of II sepd. from more concd. solns. is 7.5-9. The d.p. of the 35% soln. (satd. with II) is 7-9. During the period when the concn. of a soln. of II of d.p. 8 is increasing, primary and secondary phenomena occur. Unaltered II reaches 0.67% concn., then detaches terminal I groups until the partial tension of the I equals the d.t. of II. The following hydrolysis may occur: HO(CH₂O)₈H + H₂O → HO(CH₂O)₇H + H₂C(OH)₂ (IV); this is catalyzed by H and OH ions. Anhyd. and hydrated I and II are subsequently transformed, because the soln. must reach an equil. between the various II products, IV, and anhyd. I. These secondary reactions also are catalyzed by H and OH ions, and the rate at which concd. solns. are obtained depends on their concn. (cf. Lobering, C.A. 30, 7978.1). Solubilization proceeds by these mechanisms until the partial tension of HCHO reaches the d.t. of the sepd. II. If the initial ratio of water to II is such that this tension is not attainable, all II dissolves. But if this tension is reached with II still not in soln., other reactions take place which reduce the concn. With respect to soln. of II having d.p. 50, the same phenomena are observed, except that when the soln. is satd. with II and the partial tension of I equals the disson. tension of the ppt., the latter does not "age", because at equil. the soln. is not satd. with higher polymers. The total concn. at equil. is a function of the concn. of anhyd. I, i.e., of the tension of the insol. component. Hence, the concn.-time curve has no max. In practice, certain divergences from these phenomena are to be expected for reasons which are discussed.
 ACCESSION NUMBER: 1954:52799 CAPLUS
 DOCUMENT NUMBER: 48:52799
 ORIGINAL REFERENCE NO.: 48:9318d-1,9319a-e
 TITLE: The system: water-formaldehyde. V. Preparation of pure solutions of formaldehyde, and the separation and redissolution of polyoxymethylenes
 AUTHOR(S): Illiceto, Antonio
 CORPORATE SOURCE: Univ. Padova, Italy
 SOURCE: Gazzetta Chimica Italiana (1953), 83, 18-27
 CODEN: GCITA9; ISSN: 0016-5603
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 Ketols (0.2 mole in 150 ml. EtOH) were hydrogenated in the presence of 10 g. Pt-activated Raney Ni and 0.1 ml. 10N Na₂CO₃ soln. at atm. pressure to give from: II, 92% MeCH(OH)CHMeCH₂OH, b₁₄ 102-3°, I, 70% MeCH(OH)CH₂CH(OH)Me, b₁₇ 103°, EtCH(OH)CH₂Ac, 78% EtCH(OH)CH₂CH(OH)Me; iso-BuCH(OH)CH₂Ac, 90% iso-BuCH(OH)CH₂CH(OH)Me, b₁₆ 113°, d₂₁ 1.036, n_D 1.441; VI, 80% MeCH₂(OH)CHMeCH(OH)Me, b₁₀ 103-5°; AcCHEtCH(OH)Me, MeCH₂(OH)CHEtCH(OH)Me, b. 208°; AcCHMe₂CH(OH)Me, incomplete reaction because of steric hindrance; Me₂C(OH)CH₂Ac, 82% Me₂C(OH)CH₂CH(OH)Me, b₁₂ 102°; EtCOCH₂CH(OH)MeEt, 91% EtCH(OH)CH₂CH(OH)MeEt, b₁₂ 112-14°, d₂₁ 1.032, n_D 1.439; PrCOCH₂CH(OH)PrMe, PrCH(OH)CH₂CH(OH)PrMe, b₁₅ 110° (slow reaction); and iso-PrCOCH₂CH(OH)MePr-iso, -iso-PrCH(OH)CH₂CH(OH)MePr-iso, -, slower reaction than preceding because of greater hindrance. Distinction between intra- and intermol. H-bonding in a β-ketol was made on the basis of modifications of infrared spectra caused by (1) diln. with an inert solvent, and (2) admixt. with a compd. capable of assocn. with the ketol. p-ClC₆H₄OH was the most effective assocn. type indicator. Examn. of 14 β-ketols (primary, secondary, and tertiary) indicated intermol. assocn. Infrared analysis indicated reduction in intermol. assocn. of AcCHRCH(OH)Me as R increased from H to Me to Et, of AcCHRCH₂OH as R increased from H to Et but little further change as R increased to Bu and Am, and of MeCR(OH)CH₂CO₂R as R increased from Me to iso-Pr. Disson. of AcCHMe₂CH₂OH was much more important than that of the secondary ketols.
 ACCESSION NUMBER: 1954:6997 CAPLUS
 DOCUMENT NUMBER: 48:6997
 ORIGINAL REFERENCE NO.: 48:1250g-1,1251a-h
 TITLE: β-Hydroxy carbonyl formation and contribution to the study of steric effects
 AUTHOR(S): Dubois, J. E.
 SOURCE: Ann. chim. (Paris) (1951), 6, 406-86
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 AB Chromones unsubstituted in the 2- and 3-position yield with CH₂O and secondary amine HCl salts 3-(dialkylaminomethyl)chromone HCl salts (I); 2-methylchromones do not give this reaction. To 6.9 g. Na sand and 43.8 g. (CO₂Et)₂ in 100 cc. dry dioxane was added slowly with stirring 16.6 g. 2,5-HD(MeO)CGH₃Ac in 50 cc. dioxane, the mixture stirred 2 hrs., 10 cc. EtOH and then 15 cc. AcOH added, the resulting stiff paste diluted with 900 cc. H₂O, the solution extracted 24 hrs. with Et₂O, the extract evaporated, the residue dissolved in 200 cc. Et₂O, the Et₂O solution washed with 80 cc. 10% NaHCO₃ solution and two 50-cc. portions of H₂O, dried, evaporated, the residue dissolved in 125 cc. EtOH and 125 cc. concentrated HCl, refluxed 1 hr., and the solution cooled and filtered to yield 10.4 g. (47%) 2-carboxy-6-methoxychromone, m. 269° (decomposition) (from EtOH), which, heated at about 350° until the CO₂ evolution ceased and distilled, gave 5.1 g. (29%) 6-methoxychromone, m. 93-5° (from 50% aqueous EtOH). Similarly was prepared 2-carboxy-7-methoxychromone, decarboxylated at about 265°. A chromone (0.05 mole), 0.052 mole dialkylamine-HCl, 3 g. paraformaldehyde, and 16 cc. absolute EtOH refluxed 4-5 hrs. gave the I. By this method were prepared the following chromone-HCl's: 3-(dimethylaminomethyl) (II), 60%, m. 238-9° di-Et analog, 7.5%, m. 167-8°; 3-(piperidinomethyl), 14%, m. 262-3°; and (morpholinomethyl), 20%, m. 244-6°. Similarly were prepared from the corresponding substituted chromones the following-substituted II (substituent given): 6-MeO (III), 22%, m. 234-6°; 7-MeO (IV), 47%, m. 235-6°; 6-Me, 21%, m. 230-1°; and 6-Cl, 46%, m. 243-5°. Similar Mannich reactions with EtOCH:CHCOPh and EtOCMe:CHCOPh gave gummy, gelatinous nonbasic materials. Hydrogenation of 2 g. IV in 100 cc. 95% EtOH with 0.1 g. PtO₂ at 50 lb./sq. in. gave 3-dimethylaminomethyl-7-methoxy-4-chromanone-HCl, m. 168-70°. 2-methyl-6-methoxychromone (V) (5 g.) and 5 g. N-bromosuccinimide in 50 cc. CCl₄ refluxed 3 hrs. with stirring gave 1.3 g. (17%) 2-bromomethyl-6-methoxychromone (VI), tan needles, m. 124-6° (from EtOH). VI (5.9 g.) and 2 g. Me₂NH in 100 cc. EtOH heated 6 hrs. in a bomb with shaking at 95-105°, the EtOH evaporated, the residue taken up in 100 cc. H₂O and 200 cc. Et₂O, the mixture filtered and the Et₂O layer dried and treated with dry HCl gave 0.05 g. III, m. 223°. To 12.5 g. V in boiling 600 cc. AcOH was added at once with stirring 2.35 g. MnO₂ and 4.32 g. Br, the mixture refluxed 15 min. the cooled solution decanted from the unreacted MnO₂, and the AcOH removed in vacuo to give 2-dibromomethyl-6-methylchromone, silvery crystals, m. 158.5-60° (from EtOH). A similar Mannich reaction on 5 g. 4-pyrone gave 2 g. of an unidentified, white, crystalline solid, m. 206°. ACCESSION NUMBER: 1953:51550 CAPLUS DOCUMENT NUMBER: 47:51550 ORIGINAL REFERENCE NO.: 47:87431,8744a-e TITLE: Chromones in the Mannich reaction AUTHOR(S): Wiley, Paul F. CORPORATE SOURCE: Lilly Research Labs., Indianapolis, IN SOURCE: Journal of the American Chemical Society (1952), 74, 4326-8 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal LANGUAGE: Unavailable

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 AB α-Substituted acroleins are prepared by passing a mixture of an aldehyde and HCHO into the molten salt of a primary or secondary amine. Into 7 moles Me₂NH₃Cl containing an emulsifying agent at 200° is slowly passed a 1:1:1.0 mixture of HCHO and PrCHO, N added during the reaction period, and the products condensed, washed, seph., and distilled to give 51% EtC(:CH₂)CHO. ACCESSION NUMBER: 1951:6295 CAPLUS DOCUMENT NUMBER: 45:6295 ORIGINAL REFERENCE NO.: 45:11581,1159a TITLE: Acroleins INVENTOR(S): Bortnick, Newman M. PATENT ASSIGNEE(S): Rohm & Haas Co. DOCUMENT TYPE: Patent LANGUAGE: Unavailable FAMILY ACC. NUM. COUNT: 1 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2518416		19500808	US	

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 AB Comps. of the type ROOCR1(CH₂NR₂)CO₂R₃ (I), where R is alkyl or aryl and R₁, R₂, and R₃ are the same or different alkyl radicals, are prepared by the condensation of ROOCHR1CO₂R₃ with HCHO and a secondary amine. The I are reduced to the corresponding alc. and esterified with an acid halide to yield products of the type RCH(OCOR₄)CR1(CH₂NR₂)CO₂R₃, where R₄ is an aryl radical. Cold aqueous 35% HCHO 22 is slowly added to a cold mixture of AcCHETCO₂Et 40 and Et₂NH 18 g., the resulting mixture clarified with 50 cc. of MeOH, the product neutralized after 1 hr. with 40 g. of 25% HCl, extracted with Et₂O, the aqueous layer treated with 70 g. of 30% aqueous KOH, and the alkaline solution extracted with Et₂O; distillation of the extract yields Et α-(diethylamino-methyl)-α-ethylacetoacetate (III), b₁₉ 136-8°. Similarly are prepared Et α-diethylaminomethyl-α-methylacetoacetate, b₁₉ 129°; Et α-dimethylaminomethyl-α-ethylacetoacetate, b₁₉ 108-10°; Et α-dimethylaminomethyl-α-methylbenzoylacetoacetate-HCl, m. 146-7°; and Et α-ethyl-α-(1-piperidylmethyl)-benzoylacetoacetate-HCl, m. 144-5°. Reduction of II with 4 equivs. Al-Hg gives the unstable Et α-diethylaminomethyl-α-ethyl-β-hydroxybutyrate (III), b₁₉ 146°. III with R₄COCl yields the corresponding Bz ester (IV), m. 33° (HCl salt, m. 138°); p-nitrobenzoyl ester-HCl, m. 161°. The latter on hydrogenation gives the p-aminobenzoyl ester (V), m. 194°, HCl salt, m. 198-9°. IV and V are local anesthetics. ACCESSION NUMBER: 1953:3407 CAPLUS DOCUMENT NUMBER: 47:3407 ORIGINAL REFERENCE NO.: 47:606e-h TITLE: α-Dialkylaminomethyl-β-keto esters PATENT ASSIGNEE(S): Luxema, Societe anon., Ste. Holding Luxembourgeoise DOCUMENT TYPE: Patent LANGUAGE: Unavailable FAMILY ACC. NUM. COUNT: 1 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 666590		19520213	GB	

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 AB According to Mannich and Hof (C.A. 22, 590) EtAc and HCHO in the presence of Me₂NH give a mixture of Me₂NCH₂CH₂CO₂Et (I) and AcCHMeCH₂NMe₂ (II), whereas, according to H., et al. (C.A. 39, 2334.8; 40, 6050.3), EtAc and HCHO in the presence of alkali or HCl give 3-condensation products. Repetition of M. and H.'s experiment shows that not I but AcC(CH₂NMe₂)₂Me (III) is formed. This is proven by the fact that III requires 2 mols. HCl for neutralization, gives a pos. CHI₃ test with NaOI in MeOH-KOH, a dipicrate, m. 106-8°, and a picrolonate, m. 184°. Refluxing 20 g. BzH and 70 g. EtAc 3 hrs. with 0.8 g. piperidine (IV), distilling off the EtAc, dissolving the residue in ether, washing the ether extract with HCl, and distilling the residue of the ether solution give PhCH:CHCO₂Et, b₂₀ 160-5°, m. 37°, gives a neg. CHI₃ test. Refluxing 132 g. PhCH:CHCHO and 288 g. EtAc 6 hrs. with 5 g. IV and distillation of the reaction product give a fraction, b₁₅ 170-90°, from which is isolated 1.5 g. AcC(:CHCH:CHPh)Me, m. 69-70° (phenylhydrazine, m. 167-9°; semicarbazone, m. 225-7°). In the condensation of EtAc with aldehydes in the presence of secondary amines 1- as well as 3-condensation products may be formed, depending upon the structure of the aldehyde. ACCESSION NUMBER: 1950:37940 CAPLUS DOCUMENT NUMBER: 44:37940 ORIGINAL REFERENCE NO.: 44:7228f-1 TITLE: Condensation of butanone with aldehydes AUTHOR(S): Haessler, Herbert; Schacht, Wilhelm CORPORATE SOURCE: Tech. Hochschule, Hannover, Germany SOURCE: Chemische Berichte (1950), 83, 129-30 CODEN: CHBEAM; ISSN: 0009-2940 DOCUMENT TYPE: Journal LANGUAGE: Unavailable

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 AB Primary and secondary phenylamines and subresinous tertiary polyphenylamines are obtained by treating thiophene (I) or its alkyl derivs. 1.5-3 hrs. at 65° or reflux temperature with either an NH₄ halide and HCHO or hexamethylenetetramine and HCl. Primary and secondary amines can replace NH₄Cl but (NH₂CH₂)₂, urea, or thiourea do not give the corresponding products. I with aqueous HCHO and NH₄Cl gives 2-phenylamine (II), di-2-phenylamine (III), and a polymeric amine (IV) containing the grouping -CH₂N(CH₂OH)CH₂- or HOCH₂(CH₂)₂CH₂N-, which on heating liberates H₂O and forms resinous products. Tabulated data on the effect of the mol. ratios of reactants on the reaction products indicate that an excess of I or NH₄Cl minimizes the formation of IV and that IV is formed from the secondary amine since the yield of the 2 compds. varies in inverse proportion. For high yields of primary and secondary amines at least 2 mols. NH₄Cl/mol. I should be used. The utilization of I, aqueous HCHO, and NH₄Cl appears to be independent of the mol. ratio of the reactants and is 1:2:1, but the mol. weight of IV varies with the mol. ratio of the reactants. NH₄Cl 1.03, I 2.0, and HCHO (in the form of 37% aqueous HCHO) 1.23 mols. were heated 3 hrs. at 74°, the unreacted I decanted, EtOH added to the reaction mixture which was then filtered, freed from EtOH by evaporation, the residue neutralized with KOH solution, extracted with C₆H₆, the solvent removed, and the residue distilled in vacuo to give 9 g. II, b₅ 55-65°, n_D20 1.5650, 8 g. III, b₇ 115-45°, n_D20 1.5914, and 25 g. residue; the properties of several derivs. of II are listed. I, 2, hexamethylenetetramine 0.5, and aqueous HCl 2 mols. were kept 45 min. at 76-80°, I removed by distillation, and the mixture worked up as before, yielding II 33.0 and III 16 g. Bu₂NH 1, concentrated HCl 1, I, and HCHO 1 mol. heated 6 hrs. at 80° gave after neutralization a product, b. 298-308°, containing 21.3% S and 8.67% N. No reaction took place on heating I with paraformaldehyde and NH₄Cl but formation of II, III, and IV occurred after addition of AcOH to the reaction mixture, demonstrating the need for a depolymerizing agent for paraformaldehyde. Further examples are given which show the effect of the mol. ratio of the reactants on the production of IV. The main uses for II and III are as bearing-corrosion inhibitors for engine lubricants, but they are also suitable as intermediates for the manufacture of dyes, pharmaceuticals, or as insecticides.

ACCESSION NUMBER: 1950:22717 CAPLUS
 DOCUMENT NUMBER: 44:22717
 ORIGINAL REFERENCE NO.: 44:4509-1, 4510a-d
 TITLE: Phenylamines
 INVENTOR(S): Hartough, Howard D.; Lukasiewicz, Sigmund J.
 PATENT ASSIGNER(S): Socony-Vacuum Oil Co., Inc.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2497067		19500214	US	

L19 ANSWER 54 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 oil; this is also the final product of decompn. of VII, VIII, and X. On standing XIII evolves NH₃ and gives the compd., C₅H₁₁O₃N₂ (XIV), m. 98°; it does not contain primary or secondary NO₂ groups; with alkali it gives NH₃, and with concd. EtOH-HCl, HCHO and the HCl salt of XIII result; the mother liquor from XIV yields 104 (on basis of XIII) of a strongly alk. oil (piperidine odor), C₁₀H₂₀O₄N₄, b₁₆ 160°, n_D22 1.4862; it does not form a cryst. picrate or methiodide. III in concd. HCl, evapd. to a sirup, yields the HCl salts of V, IX, XI, and the HCl salt of HOCH₂CEt(NO₂)CH₂NHCH₂OH, sepd. by crystn. from EtOH and ether. IX was not obtained from IV.

ACCESSION NUMBER: 1948:778 CAPLUS
 DOCUMENT NUMBER: 42:778
 ORIGINAL REFERENCE NO.: 42:175a-i, 176a-b
 TITLE: Reaction of 1-nitropropane with formaldehyde and ammonia
 AUTHOR(S): Hirst, E. L.; Jones, J. K. N.; Minahan, S.; Ochynski, F. W.; Thomas, A. T.; Urbanski, T.
 CORPORATE SOURCE: Royal Arsenal, Woolwich, UK
 SOURCE: Journal of the Chemical Society, Abstracts (1947) 924-8
 CODEN: JCSAAZ; ISSN: 0590-9791
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 54 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diagram(s), see printed CA issue.
 AB PrNO₂ (89 g.) in 225 cc. 40% HCHO and 59 cc. 33% NH₄OH, stirred 12-15 hrs. at room temperature, gives an oily precipitate containing EtCH(NO₂)CH₂OH; addition of NaCl to the aqueous solution gives 100 g. of the additive compound, (C₅H₁₁O₃N₂)₃.C₅H₁₁O₃N₂ (I), of HOCH₂CEt(NO₂)CH₂OH (II) and (CH₂)₆SN₄, m. 117°, 1 results also (4.2 g.) from 4.47 g. II and 1.4 g. (CH₂)₆SN₄ in concentrated aqueous solution; it is dissociated in solution; on heating it forms a resin. PrNO₂ (89 g.), 225 cc. 40% HCHO, and 59 cc. 33% NH₄OH, stirred 15-30 min. at 90-5°, the product poured onto ice, and the oily layer reheated 8 hrs. at 90-5°, give 110-25 g. of resin A (III); similarly, 149 g. II gives 110 g. of resin B (IV), a colorless and odorless viscous liquid. Distillation of III and IV under reduced pressure gives EtCH(NO₂)CH₂OH, an unidentified blue NO derivative, and fractions b₀.01 140°, n_D16 1.4720, and b₀.01 160-80°, n_D16 1.4880; these contain 5-nitro-5-ethyltetrahydro-1,3-oxazine (V), H₂C.NH.CH₂.O.CH₂.CEtNO₂, n_D18 1.4873 (HCl salt, m. 203° (decomposition)), picrate, pale yellow, m. 156°. V and MeI give 5-nitro-3-methyl-5-ethyltetrahydro-1,3-oxazine-MeI (VI), m. 218° (decomposition); VI results also from III or IV and MeI; picrate m. 210°. VI with Ag₂O yields the hydroxide which decomposes violently on distillation, giving Me₂NH (identified as the picrate), a 2nd base which with MeI yields a derivative m. above 300°, and an aldehyde or ketone whose 2,4-dinitrophenylhydrazone, C₁₁H₁₄O₄N₄, m. 166°. Steam distillation of 9.3 g. III or IV yields 6 g. of an oil (mainly V); extraction of the aqueous distillate with ether and C₆H₆ gives 5-nitro-5-ethyl-3-(2-nitro-2-(hydroxymethyl)butyl)tetrahydro-1,3-oxazine (VII), H₂C.CEt(NO₂).CH₂.O.CH₂.NCH₂(NO₂)EtCH₂OH, m. 101°. PrNO₂ (89 g.), 225 cc. 40% HCHO, and 59 cc. 33% NH₄OH, heated 1.5 hrs. at 90-5°, give 15-20 g. 5,7-dinitro-3-(hydroxymethyl)-5,7-diethyl-1-oxa-3-azacyclooctane (VIII), O₂NCH₂.CH₂.N(CH₂OH).CH₂.O.CH₂.CEtNO₂.CH₂.m. 97°; cold concentrated HCl gives the HCl salt, m. 174°, which is hydrolyzed by cold H₂O. VIII, warmed with concentrated HCl, loses 1 mole HCHO and yields the HCl salt (IX), m. 197°, of N-(hydroxymethyl)-2,4-dinitro-4-(hydroxymethyl)-2-ethylphenylamine, HOCH₂CH₂(NO₂)EtCH₂(NO₂)EtCH₂NHCH₂OH (X), an oil. IX, heated with aqueous HCHO, yields VIII. With NaNO₂ IX gives an oily NO derivative which regenerates IX with concentrated EtOH-HCl. The picrate of X, pale yellow, m. 154°, could not be crystallized from H₂O. Distillation of X yields V and EtCH(NO₂)CH₂OH. II (149 g.), 75 cc. 40% HCHO, and 26 cc. 33% NH₄OH, heated 1.5 hrs. at 95-6°, give 50 g. VII; it can be prepared from IV by solution in cold concentrated HCl, pouring onto ice, and extracting the resinous precipitate with ether. With cold concentrated HCl, VII yields the HCl salt, m. 156°; it results also by passing HCl through VII in CHCl₃ or CCl₄; it is hydrolyzed by H₂O. VII (or its HCl salt), heated with concentrated HCl, loses 1 mole HCHO and is converted to the HCl salt (XI), m. 186°, of bis[2-nitro-2-(hydroxymethyl)butyl]amine (XII), NH(CH₂CEt(NO₂)CH₂OH)₂, m. 54° (picrate, m. 148°). XI and aqueous HCHO give VII. The oily NO derivative regenerates XI with concentrated HCl. On boiling XII in H₂O 2 moles HCHO are liberated. Distillation of XII gives V, EtCH(NO₂)CH₂OH, and unchanged XI. The HCl salt of V, boiled with H₂O, gives 1 mole HCHO and the HCl salt, m. 126°, of 2-nitro-2-(hydroxymethyl)butylamine (XIII), an

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 AB An investigation is reported of the manner in which the hydroxyphenyl group of tyrosine (I) might react with HCHO, as well as the stability to acid hydrolysis of any linkages that might be thus formed. I (80 g.) in 323 cc. 2.74 N NaOH was treated with 26.6 g. HCHO and the mixture kept at 20° for 10 days; the filtrate was adjusted to pH 5.5 with HCl and the precipitate was purified by solution in N NaOH and precipitation at pH 5.5. The optical rotation of the solution (followed for 40 days) and the decrease in free HCHO indicate that 1 mol. of HCHO is taken up rapidly and a 2nd mol. much more slowly. The reaction product (II) (C₁₁H₁₃NO₄)_x, is amorphous, [α]_D25 18.1° (3 N NaOH, c 0.9), solubility in H₂O 0.01%, readily soluble in alkali than in acid. Air-dried II heated at 105° continues to lose weight slowly. X-ray diffraction patterns of II indicated its amorphous nature. The absorption maximum of II is at 284 m., sp. extinction coefficient 9.81. Electrophoretic patterns of II in barbitol buffer at pH 7.8 show 2 definite peaks; heterogeneity of II was substantiated by fractionation of an alkaline solution with dilute acid; although the larger portion precipitated at pH 5.5, small fractions were obtained at pH 4.5 and 3.5. Dialysis of II against distilled H₂O for 6 days yielded none of the material in the dialyzate. Hydrolysis of II with N acid for 7 hrs. liberated no HCHO. II contains no amino N; that the N of II is secondary rather than tertiary was shown by the fact that addition of HCHO to an aqueous alkaline solution caused a drop in pH. When heated at 105°, II becomes less soluble in 0.1 N NaOH but is not resinsified. When heated with catalytic quantities of NaOH or NH₃, II gives light-brown, transparent, somewhat brittle resins; HCl gives a tough, opaque resin. Acetylation of II gives products containing 4.7 to 5.9% N. Inorg. salts, picrates, and methylated derivs. do not have constant compns.

ACCESSION NUMBER: 1946:24996 CAPLUS
 DOCUMENT NUMBER: 40:24996
 ORIGINAL REFERENCE NO.: 40:4911a-e
 TITLE: Polymer reaction product of tyrosine and formaldehyde
 AUTHOR(S): Brown, Alfred E.
 CORPORATE SOURCE: Eastern Regional Research Lab., Philadelphia
 SOURCE: Journal of the American Chemical Society (1946), 68, 1011-15
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 56 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB A secondary aliphatic alc. 2 mols. are refluxed with CH₂O (as aqueous solution or paraformaldehyde) 1-20 mols. and a strong acid 3-50% until at least 10% of a H₂O-insol. condensation product is formed, boiling at least 20° above the corresponding formal and having a d. at least 3% greater. Thus refluxing sec. C₇H₁₅OH 116, 40% aqueous CH₂O 85 and 47% H₂SO₄, 40 parts for 1 hr., separating and drying the nonaq. layer, and distg. gave 140 parts of product, 2/3 of which boiled 150-260°. Some of the products are nitrocellulose solvents.

ACCESSION NUMBER: 1946:7743 CAPLUS
 DOCUMENT NUMBER: 40:7743
 ORIGINAL REFERENCE NO.: 40:1354h-1
 TITLE: Reaction products of secondary aliphatic alcohols and formaldehyde
 INVENTOR(S): Harvey, Mortimer T.
 PATENT ASSIGNMENT(S): Harvey Research Corp.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2388409		19451106	US	

L19 ANSWER 58 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 GI For diagram(s), see printed CA Issue.
 AB Unlike secondary amines, primary amines, such as MeNH₂, react only poorly with HCHO and ketones to form 1,3-keto bases with a secondary N atom, and only with special ketones like Et₂CO or MeCOPh (Mannich and Heilner, C. A. 16, 2497). With PhCH₂NH₂.HCl (or 3,4-CH₂O₂C₆H₃CH₂NH₂), however, there is obtained with HCHO and ketones, such as cyclohexanone (II), acetone, PhCH₂CHCOMe, 1-tetralone, PhCOMe and cyclopentanone, up to 65% of the corresponding keto bases: PhCH₂NH₂.HCl + HCHO + RCH₂COMe → H₂O + PhCH₂NHCH₂CHCOMe.HCl. In these 1,3-keto bases, unlike the 1,3-amino alcs. obtained by their reduction, the PhCH₂NH residue is loosely held. In the hydrogenation of II under pressure and at elevated temps. PhCH₂NH₂ is often formed along with the alc. base. As byproducts in the preparation of 1,3-keto bases there are also formed tertiary bases when a double amount of HCHO is used; they are also formed from 1 mol. PhCH₂NH₂, 2 mols. HCHO and 2 mols. ketone, "ketol condensation" occurring with formation of a piperidine or isoquinoline ring. The tertiary base obtained by M. and Heilner from MeNH₂, CH₂O and PhCOMe is likewise to be regarded as a keto alc. base, not as a diketo base; its reduction product is not a pinacol but a secondary-tertiary glycol. Some of the products obtained are alkaloid-like, such as 2-benzyl-4-acetyl-10-hydroxydecahydroisoquinoline or 2-(3,4-methylenedioxybenzyl)-4-acetyl-10-hydroxydecahydroisoquinoline, and possess, along with low toxicity, spasmolytic properties; the latter of the 2 compds. is half as effective as papaverine. Attempts to use, instead of ketones, appropriate aldehydes (e. g., 1,3o-PhCHO) are being made. 2-(Benzylaminomethyl)cyclohexanone (II); 36 g. PhCH₂NH₂.HCl (III), 20 g. of 40% HCHO (IV) and 74 g. I were heated and, after the reaction had subsided, were again brought to a boil, 5 g. IV was added to bind unreacted III, the excess of I distilled off, the residue dissolved in 100 cc. water, the solution made alkaline after extraction with ether, again extracted with ether, the extract shaken out with just enough 20% HBr, the salt solution concentrated somewhat in vacuo, the HBr salt of the tertiary amine (V), m. 186° (about 10% yield) separated, the filtrate evaporated and the residue crystallized from AcOEt. The HBr salt of II m. 129° (65% yield); oxime, needles, m. 85°; N-Bz derivative, m. 134°. N-Carboxy derivative, from the free II and ClCO₂Et in pyridine, oil with bitter taste, b11 222°. 2-(Benzylaminomethyl)cyclohexanol, from III in water kept acid with HCl and Na-Hg, precipitated with KOH and distilled in vacuo, b16 194-7°. After neutralization with HBr there seps. the α-form of the HBr salt, m. 160-1° (from acetone), while the β-form, after separation of the α-HBr salt, is precipitated as the free base, distilled and isolated as the HCl salt, m. 144°. HCl salt of the α-form, m. 160°. Bz derivative of α-form, m. 159-60°; of β-form, m. 148°. 2-Oxo-3-benzyldecahydroquinazoline, from II, HBr with KCN by spontaneous cleavage of water from the intermediate, nonisolable urea derivative, m. 191° (from alc. or AcOEt). It is disproportionated by boiling 20% HCl on concentration and addition of water 2-oxo-3-benzyldecahydroquinazoline, m. 175° (from alc.), ppts. and evaporation of the filtrate yields the HCl salt of the hexahydro compound, yellow needles from 25% acetone, m. 212°; free base, m. 153°. The tertiary base V is also obtained in up to 25% yield from III, IV and I in the mol. ratio 1:2:1. After separation of II as the quinazoline with KCN,

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 AB cf. C. A. 39, 1899.3. This work was undertaken when it was observed that gliadin and wheat gluten bound more HCHO than did other proteins after treatment with 4% HCHO at 70° and pH 3-7. It was possible to demonstrate that the primary amide as well as the NH₂ groups of proteins bound aldehyde under these conditions. The secondary amides of the peptide chain did not react appreciably with HCHO. In most expts. 1 g. of protein or polypeptide in 8 ml. of H₂O was treated with 1 ml. of buffer and 1 ml. of 37-8% HCHO and kept at 70° for 4 days (intermittent shaking); the aldehyde contents of the final products varied by no more than 10% with the different techniques of isolation. Of the final amount of HCHO, 50% was bound in 8 hrs. and 90% in 24 hrs. Lysozyme bound about 37% more HCHO at pH 6.8 than at pH 3.8; egg-white protein 18% more, gluten 10% more, zein the same amount at both pH levels, and polyglutamine 38% less at the higher pH. The HCHO concentration and the reaction temperature affect the maximum amount of HCHO introduced; gluten bound about 2% of its weight of HCHO when treated at room temperature with 3.8% HCHO or at 70° with 0.75% HCHO; the use of 18% HCHO at 70° (pH 3.8) introduced 7% of HCHO as compared with 6% from 3.8% HCHO. The HCHO retained by the proteins after the usual washing procedure was comparatively stable during further prolonged contact with H₂O at room temperature. Steam distillation caused the release of most of the bound HCHO. Heating the dry material at 100° for 7 days reduced the HCHO content by 60-70%; at 150° for 3 days, by 85%. Exhaustive washing of aldehyde-treated proteins with Na₂SO₃ is not a suitable technique for removal of unbound HCHO. Details are given of the preparation of polyglutamic acid, its Me ester, and polyglutamine. The moles of aldehyde bound at pH 3.5-4 and 70° per 104 g. of protein, etc. (values are given also for primary NH₂, total basic, and primary amide groups) are: polyglutamine 47, gliadin 23 (PhNCO-treated, 9), gluten 20 (HNO₂-treated 4, PhNCO-treated 5), lysozyme 13, zein 15 (HNO₂-treated 8), casein 12 (HNO₂-treated 6), hoof powder 12, egg-white protein 11 (PhNCO-treated 4), egg albumin 9, wool keratin 11, feather keratin 8, gelatin 6, polyglycine 3, polyglutamic acid 2.6, silk fibroin 2.3, nylon 0.3. The amino-N contents of the treated proteins were reduced to 10-20% of the starting materials. There is a correlation between the sum of the basic and the amide groups of proteins and their capacity to bind HCHO; thus, these groups are responsible for a great part of the HCHO bound by proteins under the conditions used.

ACCESSION NUMBER: 1945:20833 CAPLUS
 DOCUMENT NUMBER: 39:20833
 ORIGINAL REFERENCE NO.: 39:33151,3316a-f
 TITLE: Reaction of CH₂O with proteins
 AUTHOR(S): Fraenkel-Conrat, Heinz L.; Cooper, Mitzi; Olcott, Harold S.
 SOURCE: Journal of the American Chemical Society (1945), 67, 950-4
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 58 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 is pptd. with KOH and crystd. from MeOH; free base, m. 102°; HBr salt, m. 186°; HCl salt, m. 176°; oxime, m. 186°. With Na-Hg in dil. AcOH V gives the diHO base, m. 162° (from MeOH); diacetate, m. 154° (from MeOH). 2-Benzyl-4-acetyl-10-hydroxydecahydroisoquinoline (VI): After 5 h. boiling of 12 g. II, HBr, 1.2 g. paraformaldehyde, 50 cc. acetone and a few drops of HCl (mxt. acid to Congo) and 3 h. boiling after addn. of another 1.2 g. paraformaldehyde, distn. of the acetone, and addn. of 40 cc. water, ice-cold KOH ppts. 8 g. VI, m. 96° (from petr. ether); HCl salt, m. 195°; oxime, m. 131°. 2-Benzyl-4-(1-hydroxyethyl)-10-hydroxydecahydroisoquinoline was obtained from VI by hydrogenation with Pt oxide in alc. as the HCl salt, m. 240-1° (from abs. alc.); free base, needles, m. 115-17° (from petr. ether). 2-Benzyl-4-acetyloctahydroisoquinoline: The tertiary HO group of VI is split off as water with concd. H₂SO₄; the cleavage may occur in different directions. The mxt. from 2 cc. concd. H₂SO₄ and 1 g. VI was poured after 3 days into NaOH, the free base extd. with ether, the ether neutralized with HClO₄, the residue from the ether treated with alc. and cooled with ice, after sepn. of 0.2 g. perchlorate A (m. 146°) the residue was dissolved in hot water; cooling gave 0.1 g. perchlorate B, m. 201°. Hydrogenation of the free bases from perchlorates A and B in alc. with Pt oxide gave 2-benzyl-4-acetyloctahydroisoquinoline; acid oxalate, m. 156°. 2-Benzyl-4-benzoyl-10-hydroxydecahydroisoquinoline (VII), obtained as the HCl salt with 1 mol. H₂O from II by heating with ClCH₂CH₂CO₂H in alc. (yield, 50%), m. 212°; free base, m. 164° (from ligroin). VII is also obtained from PhCH₂NH₂.HBr, MeCOPh and IV in dioxane. 2-Benzyl-4-benzoyloctahydroisoquinoline, obtained from VII treated with concd. H₂SO₄, poured into NaOH and extd. with ether, tables, m. 97° (from alc.). 1-Benzylamino-3-oxobutane (VIII), obtained as the HCl salt from III (soln. acid to Congo), paraformaldehyde and acetone by boiling, distn. and recrystn. of the residue from acetone, leaflets, m. 162°; HBr salt, m. 124-6° (from acetone); free base, b6 155°; oxime 0 HCl salt, needles from water, m. 151°; urea deriv., from the HCl salt with concd. KCN, white needles, m. 120-1° (from MeOH). 1-Benzylamino-3-hydroxybutane (IX), b2 122-3°, was obtained by redn. of VIII in weakly acid soln. with Na-Hg, ppts. with KOH and distn.; HBr salt, m. 57° (from acetone). p-O₂N₂C₆H₄COCl in CHCl₃ with VIII gives a mxt. of the N-p-nitrobenzoyl compd., pale yellow leaflets, m. 236°, and the corresponding HCl salt, white leaflets, m. 191°. 1-Benzylamino-3-bromobutane was obtained in 18 g. yield, from 15 g. IX and 75 g. of 66% HBr heated 8 h. in a tube at 160° and treated with water, as the HBr salt, colorless needles, m. 212° (from acetone). The free base did not condense with CHNA(CO₂Et)₂ but split off HBr with formation of 1-benzylamino-2-butene, b12 95°. HCl salt, white leaflets, m. 134-5°. The base was hydrogenated to PhCH₂NH₂.HBr; HCl salt, m. 242°. 1-Benzyl-4-hydroxy-4-methyl-5-acetylpiperidine (X): From 70 g. VIII, -HCl, 20 g. paraformaldehyde and 450 cc. acetone there was obtained, after boiling 10 h., distg. off the acetone, taking up in 1.5 l. water and ppty. with KOH, a thick oil, probably the stereoisomeric forms of X, which after redn. with Na-Hg yielded a mxt. of the 2 forms of 1-benzyl-4-hydroxy-4-methyl-5-(1-hydroxyethyl)piperidine, b12 220-5°; from this was isolated 20% of a perchlorate m. 201°; the free base from the latter b12 223° and formed a HBr salt, m. 175°, (from acetone), and a di-Ac deriv., needles, m. 129-31°. 1-Benzylamino-4-benzylidene-3-butanone (XI): Equimol. amts. of III, IV and PhCH₂CHCOMe yielded, after heating, 20% of the HCl salt of XI, m. 182-4°, difficultly sol. in acetone, and, after distn. of

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 the acetone, treatment with KOH, extn. with ether and evapn. of the ether, 5-10% of 1-benzyl-4-hydroxy-4-styryl-5-cinnamoylpiperidine, pale yellow needles, m. 148° (from acetone). The free XI m. 50-1° (from petr. ether) and changes on standing into an acid-insol. red-brown resin. Hydrogenation of XI.HCl with Pt oxide in MeOH gives the HCl salt of 1-benzylamino-4-hydroxy-1-3-butanol, m. 99-100° (from base, small needles, m. 87-9° (from ligroin). 3-(Benzylaminomethyl)-4-oxotetralin (XII) was obtained by heating equimol. amts. of 1-tetralone, III and IV as the HCl salt (yield, 55%), m. about 160° (from alc.-acetone), gives with KCN through the nonisolable urea deriv. a pyrimidine deriv., slender gleaming leaflets, m. 208° (from alc.). With NaNO₂ in HCl, XII.HCl gave 90% of the nitrosamine, needles, m. 94°, yielding on boiling with Sn and concd. HCl 2-benzyltetrahydro-6,7-bis(2-oxo-3-(3,4-methylenedioxybenzyl)-2-oxo-cyclohexylmethyl)amine (XVII) like II. The soln. of the HBr salt yielded 2 salts sepd. by hot abs. alc.: the sol. salt of the secondary base (XVI), m. 155-6°, and the slightly sol. salt of the tertiary base (5% yield), m. 250°. N-Bz deriv. of XVI, needles, m. 118°. 2-Oxo-3-(3,4-methylenedioxybenzyl)octahydroquinazoline, from XVI.HCl with KCN, needles, m. 168°. The base corresponding to V, from IV, XVII and I, forms needles, m. 167° (from MeOH). 2-(3,4-Methylenedioxybenzyl)-4-acetyl-10-decahydroisoquinoline, from XVI.HBr, paraformaldehyde and acetone, needles, m. 127° (from MeOH). 1-(3,4-Methylenedioxybenzylamino)-3-oxobutane was prepd. from XVII like VIII; HCl salt, m. 176°. 3-(3,4-Methylenedioxybenzylamino)methyl-4-oxotetralin was prepd. like XII; HCl salt, m. 19°. With KCN it gives 2-oxo-3-(3,4-methylenedioxybenzyl)naphthopyrimidine, fine needles, m. 228°. β -(3,4-Methylenedioxybenzylamino)propiphenone was prepd. like XIII; HCl salt, m. 187°; urea deriv., m. 144°. 1-(3,4-Methylenedioxybenzylamino)-4-benzylidene-3-butanone was obtained like XI; HCl salt, m. about 186°. Hydrogenation with Pt oxide gives the HCl salt of 1-(3,4-methylenedioxybenzylamino)-4-benzyl-3-butanone, m. 205°. 2-[(3,4-Methylenedioxybenzylamino)methyl]cyclopentanone, analogous to XV, needles, m. 161-2°; urea deriv., m. 160°. Benzyl (benzylamino)(2-oxocyclohexyl)-methane (XVIII): A mixt. of 2.1 g. PhCH₂NH₂ and 2.4 g. PhCH₂CHO is treated, after drying with K₂CO₃, with 6 g. l. satd. in ice, after 1 day, with HCl gas, treated after 15 days with water and extd. with ether; the ether yields 0.3 g. XVIII as the HCl salt, m. 154°.

ACCESSION NUMBER: 1943:6655 CAPLUS
 DOCUMENT NUMBER: 37:6655
 ORIGINAL REFERENCE NO.: 37:1125b-1,1126a-1,1127a-h
 TITLE: Synthesis and reactions of 1,3-ketonic bases with secondary nitrogen
 AUTHOR(S): Mannich, Carl; Hieronimus, Otto

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 SOURCE: Ber. (1942), 75B, 49-64
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 GI For diagram(s), see printed Ca Issue
 AB The object of this work was to apply the Tollens' reaction (Ann. 289, 46 (1896)) between HCHO and ketones in the presence of Ca(OH)₂ to p-amino ketones for the preparation of aminohydroxy ketones and aminopolyhydroxy compds. It seemed advisable to use an amino ketone with tertiary N to avoid the complications which might arise from the reaction of the HCHO with a primary or secondary amino group, and hence the readily available MeCOCH₂CH₂NHMe₂ (I) (C. A. 12, 684) was selected. Aqueous I reacts readily with HCHO without addition of Ca(OH)₂ being necessary; the alkalinity of the I itself is sufficient. At 0° 1 mol. HCHO is to a great extent, but not completely, used up in the course of several hrs., and from the reaction mixture there can be isolated some unchanged I, a diamine, MeCOCH₂(CH₂NHMe₂)₂ (II), and a further basic fraction (III). The formation of II shows that I partially breaks down with liberation of NHMe₂. All attempts to establish the nature of III, which presumably contained the dimethylaminohydroxy ketones sought, resulted in resinification or decomposition. Accordingly, as 1,3-amino ketones are known to be sensitive whereas the corresponding alcs. are stable, recourse was had to reduction. When a mixture of I, water and 1 mol. HCHO is acidified with HCl after some hrs. and reduced with Na-Hg there is obtained a mixture of bases which can be separated by fractional distillation into about equal parts of (1) 1-dimethylamino-3-butanol (IV), b₂ 55-65°, and (2) 1-dimethylamino-2-(dimethylaminomethyl)-3-butanol (V), b₂ 85-100°, (3) a mixture, b₂ 130-45°, of diastereomeric α - and β -1-dimethylamino-2-hydroxymethyl-3-butanols (VI), and (4) a thick oil, b₂ 180-200°, probably a mixture of dimethylaminotrihydroxyhexanes (VII), HOCH₂CH₂CH(OH)CH₂(OH)CH₂NHMe₂, one of which was isolated as a methiodide. The formation of the stereomeric VI shows that the original condensation product contained the corresponding HO ketone which, on reduction, gives 2 glycol bases because an addnl. asym. C atom is produced. Possibly a ketone, HOCH₂CH₂COCH₂CH₂NHMe₂, is also formed in small amount but the corresponding reduction product was not found. Separation of the 2 VI is difficult. α -VI can be isolated as the dibenzoate-HBr and obtained pure by saponification of this ester. The 2 HO groups can readily be replaced by Cl; the resulting α -1-dimethylamino-2-chloromethyl-3-chlorobutane (VIII) gives with MeNH₂ the triamine, MeCH(NHMe₂)CH(CH₂NHMe₂)₂ (IX) (see following abstract), b₂ 91°. β -VI has not as yet been obtained pure, but the di-Cl compound, β -VIII, has; the latter with NHMe₂ gives the same IX as does α -VIII. α - and β -VIII by ring closure give the same quaternary dimethyl(β -1-chloroethyl)trimethylammonium chloride, Me₂Cl (X), which establishes the structure MeCHClCH(CH₂Cl)CH₂NHMe₂ of the VIII, for a compound of the structure ClCH₂CH₂CHClCH₂CH₂NHMe₂, which would yield a piperidinium salt on ring closure, could not exist in 2 stereomeric forms. Moreover, that X is a trimethyleimonium salt is shown by its behavior on thermal decomposition: the ring is opened and a mixture of α - and β -VIII distills over, whereas a piperidinium salt would give MeCl and a monochloropiperidine. Fraction (4) above has a composition corresponding approx., but not exactly, to VII; Zerewitinov detns. show 3 mobile H atoms and acetylation with Ac₂O gives an oil (XI) with an AcO content agreeing with that of a triacetate: from both VII and XI, which are undoubtedly mixts. of isomers, can be isolated about 30% of homogeneous methiodides which are genetically related. For the methiodide obtained from XI gives on cautious saponification that obtained from VII.

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 Hofmann degradn., VII.MeI splits off 1 mol. NHMe₃ and gives a high-boiling, N-free, H₂O-sol., thick, very hygroscopic liq. unsatd. toward KMnO₄. α -VI, b₂ 133-5°; HI salt, m. 113°; methiodide, m. 115°; dibenzoate-HBr (XII), m. 224°. α -VIII.HCl, from α -VI and SOCl₂ in CHCl₃, m. 165°; free VIII, b₂ 80°; HBr salt, m. 164°. The mother liquors from XII, on sapon., give a mixt. of α - and β -VI in which, however, the β -form has been so concd. that it can be isolated as the methiodide, m. 140°. With SOCl₂ in CHCl₃, 9 g. of this mixt. yields about 3 g. α -VIII.HCl and 7 g. β -VIII.HCl, m. 129-31°, which gives the free β -VIII, b₂ 78°, whose HBr salt m. 148-9°. X, from α -VIII and NaI in acetone allowed to stand 8 days at room temp. or from β -VIII.HCl and KOH in ether heated 14 days at 50°, is isolated as the chloraurate, yellow, m. 133°; the hygroscopic chloride, cautiously heated in vacuo, regenerates a mixt. of α - and β -VIII. 1-Dimethylamino-2-methylene-3-chlorobutane, from X shaken with Ag₂O, filtered, evapd. in vacuo and heated higher, b₄ 86°; HCl salt, m. 179°; decolorizes aq. KMnO₄ and Br. (2-Hydroxymethyl-3,5-dihydroxyamyl)trimethylammonium iodide, VII.MeI, m. 114°. XI, b₂ 185°; methiodide, m. 173-4°.

ACCESSION NUMBER: 1939:29734 CAPLUS
 DOCUMENT NUMBER: 33:29734
 ORIGINAL REFERENCE NO.: 33:4195c-1,4196a-e
 TITLE: Dimethylaminodihydropentanes and dimethylaminotrihydroxyhexanes
 AUTHOR(S): Mannich, Carl; Salzmann, Otto
 SOURCE: Ber. (1939), 72B, 499-505
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 AB cf. C. A. 31, 2591.1. Condensation of phenolic ethers with HCHO and HCl in the presence or absence of dehydrating catalysts gives, under favorable conditions, the corresponding chloromethyl derivs. which can be converted, by treatment with NaOAc in AcOH and saponification of the resulting acetic esters by KOH in dilute alc., into methoxybenzyl alcs. This method has been applied to the Me ethers of the cresols, thymol and to nitronisole to prepare the corresponding benzyl alcs. A well-cooled mixture of 244 g. of o-MeC₆H₄OMe and 180 g. of 40% HCHO was saturated, with stirring below 5°, with a rapid current of HCl. The reaction product was treated with ice and extracted with petr. ether. The extract was washed, dried over Na₂SO₄ and evaporated. Rapid distillation gave the chloromethyl compound, 3-methyl-4-methoxybenzyl chloride, b₂₀, 119°, d₄₂₀ 1.130, n_{D20} 1.548, decomposing on heating. The crude product was therefore poured into a warm solution of 164 g. anhydrous NaOAc in 400 g. AcOH, evaporated free from petr. ether and heated for 30 min. at about 100°. The crude ester was extracted with Et₂O and saponified by boiling for 1 hr. with 100 g. KOH in 200 g. of 95% alc. and 200 g. H₂O. The solvents were evaporated off in vacuo and the crude alc. was extracted with Et₂O and fractionated, yielding 40% (125 g.) of 3-methyl-4-methoxybenzyl alc., b₁₈ 148-9°, d₄₁₆ 1.095, n_{D16} 1.5445; phenylurethan, m. 90.5°, and 74 g. of 3,3'-dimethyl-4,4'-dimethoxydiphenylmethane (cf. R. Quelet, C. A. 28, 2687.1), b₇ 193-4°, m. 24°, formed as a secondary product in the chloromethylation of o-MeC₆H₄OMe. Similar treatment of 183 g. of m-MeC₆H₄OMe, b. 174-5°, n_{D20} 1.5140, gave 140 g. of crude product which, on fractional distillation, yielded 15% (30 g.) of 2-methyl-4-methoxybenzyl alc., b₁₈ 145°, n_{D18} 1.5455 (oxidized by KMnO₄ to 2-methyl-4-methoxybenzoic acid, m. 176°, and forming a phenylurethan, m. 71°), and 80 g. of 2,2'-dimethyl-4,4'-dimethoxydiphenylmethane, m. 69°, oxidized by CrO₃ to the corresponding benzophenone, m. 72°. The poor yield of alc. is due to the instability of the chloromethyl intermediate which tends to condense with the Me cresolate to give the di-Ph derivative and with itself to form resins. A well-stirred mixture of p-MeC₆H₄OMe, 150 g. of 40% HCHO and 60 g. ZnCl₂ was saturated with HCl for 75 min. The product was washed with H₂O, shaken with dilute NaOH, re-washed, dried over Na₂SO₄ and immediately distilled, yielding 295 g. of 2-methoxy-5-methyl-α-chlorotoluene, b₁₆ 124°, d₄₁₆ 1.128, n_{D16} 1.5455, transformed by heating for 1 hr. at 100° with a slight excess of NaOAc in AcOH into the Ac derivative, C₁₁H₁₄O₃, b₁₆ 146°, d₄₁₆ 1.091, n_{D16} 1.515, which was saponified in 80% yield to 2-methoxy-5-methylbenzyl alc. C₉H₁₂O₂, b₁₆ 140-1° d₄₁₆ 1.092, n_{D16} 1.5427 (phenylurethan, m. 90°), oxidized by KMnO₄ in the cold to 2-methoxy-5-methylbenzoic acid, m. 69°. Under similar conditions Me thymate gave 60-70% of 2-methyl-4-methoxy-5-isopropyl-α-chlorotoluene, b₁₆ 148°, d₄₁₆ 1.067, n_{D16} 1.539, converted through the ester to 2-methyl-4-methoxy-5-isopropylbenzyl alc., b₁₈ 165°, d₄₁₈ 1.041, n_{D18} 1.534, crystallizing on standing for 2 months to long prisms, m. 35° (phenylurethan, m. 101°), oxidized by KMnO₄ to 2-methyl-4-methoxy-5-isopropylbenzoic acid, m. 139°. Distillation of the crude alc. preparation yielded also 2,2'-dimethyl-4,4'-dimethoxy-5,5'-diisopropylidiphenylmethane, m. 73°, oxidized by Na₂Cr₂O₇ in AcOH into colorless needles of the corresponding benzophenone, m. 139°. A mixture of 300 g. of o-nitroanisole, 220 g. of 40% HCHO and 165 g. ZnCl₂

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 GI For diagram(s), see printed CA issue.
 AB Schafer and Tollens obtained from NH₄Cl, HCHO and PhCOMe a base (I) to which they ascribed the structure (PhCOCH₂CH₂)₂NH (II). The reaction is more complicated, however: in addition to I there is formed an isomer (III), which is unstable and changes into I when boiled in alc.; a rearrangement of I into III could not be effected. It is not a question of dimorphism; I and III give the same methiodide, to be sure, but their salts (HCl, picrate, chloroplatinate, chlorosulfate) are different and cautious treatment with Ac₂O gives different Ac derivs. W. and A. suggest, with some reserve, that the stable I has the cyclic structure Ph₂CH₂CH(COPh)₂ (IV) and that it is III which has the structure II. Attempts to determine the form of union of the O atoms in I and III by oxime or semicarbazone formation gave no utilizable results; there were formed mixts. which could hardly be separated. Attempts were then made to show the presence of OH groups. PhNCO reacts with neither I nor III; BzCl converts III into I, which cannot be benzoylated (at higher temps. BzCl decomposes I with formation of Bz₃N). On short and cautious heating with Ac₂O I and III give different Ac derivs. (V and VI), while on more energetic acetylation both give the same Ac derivative (of the labile III). The 2 Ac derivs. are insol. in acids, hence the Ac group has combined with the N atom with elimination of PhCOCH₂CH₂. Here it is the acyclic form, (PhCOCH₂CH₂)₂NHAc (VI), which is the stable isomer; its structure is proved by the formation of a dioxime and a disemicarbazone. PhNCO does not react with V, but SOCl₂, which does not attack VI, replaces the HO group in V by Cl, giving a compound (VIII) which readily splits off HCl with alc. KOH, forming an unsatd. base (VIII) in which the position of the double bond is as yet uncertain. VIII takes up 1 mol. H₂ on catalytic hydrogenation, yielding a product which is apparently not homogeneous; the greater part can easily be isolated in crystalline form (IX) while the noncryst. residue is possibly a stereoisomer, since in the hydrogenation 2 C atoms become asym. S. and T. had already observed that I.HCl splits off PhCOCH₂CH₂ when distilled with steam. III.HCl behaves in the same way. The distillation residues give in good yield the HCl salt of a secondary base, (PhCOCH₂CH₂)₂NH₂ (X), stable only in the form of its salts; the free X soon disproportionates into NH₃ and I. The tendency to form I is so great that X adds PhCOCH₂CH₂ even at 15-20°. The secondary nature of X is shown by the formation of stable N-Ac and N-Bz derivs., a nitrosamine and a urea derivative; the Ac derivative is identical with VI. Its HCl salt on distillation with steam (best superheated) in dilute solution likewise slowly splits off PhCOCH₂CH₂, forming the HCl salt of a primary base, PhCOCH₂CH₂NH₂ (XI) (separated from the unchanged X.HCl only with some difficulty); the free XI, too, disproportionates into NH₃ and I. Tris(β-benzoyl-ethyl)-amine (III), m. 67°; HCl salt, m. 145°; picrate, m. 140-2°; chloroplatinate; chlorosulfate, yellow, m. 168°; methiodide, m. 147-8°. 4-Hydroxy-4-phenyl-5-benzoyl-1-(β-benzoyl-ethyl)piperidine (I), m. 150°. HCl salt, m. 199-200°; chloroplatinate, m. 207-8°; picrate, yellow, m. 154°; methiodide, identical with that of III. VI, m. 110°; dioxime, m. 210°; disemicarbazone, m. 210-12°; bis(p-nitrophenylhydrazones), m. 207-8°. V, from I heated 2-3 min. with Ac₂O on the water bath, m. 160°. VII, m. 165°. 1-Acetyl-4-phenyl-5-benzoyltetrahydropyridine (VIII), m. 143°; the piperidine (IX), m. 168°. Bis(β-benzoyl-ethyl)amine-HCl, m. 175°. chloroplatinate, m. 194-5°; chlorosulfate, m. 120°; N-Bz

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 was satd. with HCl for 1.5 hrs. with agitation. The temp. rose to 80° in 15 min. and remained between 80° and 90° during the reaction. Recrystn. of the solid product gave 375 g. of the chloride, m. 85.5-6.0°. A 90% yield (170 g.) of the acetate, m. 37°, was obtained from 160 g. of the chloride by heating for 2 hrs. at 100° with 190 g. NaOAc in 400 g. AcOH. Sapon. by agitation with concd. KOH for 24 hrs. and recrystn. of the solid product from alc. produced 92% of 3-nitro-4-methoxybenzyl alc., m. 69° (phenylurethan, m. 129°), converted by cold dil. KMnO₄ to 3-nitro-4-methoxybenzoic acid, m. 189.5°.
 ACCESSION NUMBER: 1937:61806 CAPLUS
 DOCUMENT NUMBER: 31:61806
 ORIGINAL REFERENCE NO.: 31:85209-1, 8521a-g
 TITLE: Synthesis of methoxybenzyl alcohols
 AUTHOR(S): Quelet, Raymond; Allard, Jean; Ducasse, Joseph; Germain, Yvette
 SOURCE: Bull. soc. chim. [5] (1937), 4, 1092-1101
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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 deriv., m. 105-6°; nitrosamine, m. 114-15° (decompn.); urea, m. 187° (decompn.). β-Benzoyl-ethylamine-HCl, m. 125°; chloroplatinate, m. 227-8° (decompn.); picrate, m. 160°.
 ACCESSION NUMBER: 1935:19787 CAPLUS
 DOCUMENT NUMBER: 29:19787
 ORIGINAL REFERENCE NO.: 29:25351, 2536a-1
 TITLE: The bases formed from acetophenone, formaldehyde and ammonium chloride
 AUTHOR(S): Mannich, C.; Abdullah, S. H.
 SOURCE: Ber. (1935), 68B, 113-20
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 62 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB This new synthesis consists in condensing aldehydes with HCHO and the salts of secondary amines (Me₂NH, Et₂NH, piperidine): Me₂NH + HCHO + Me₂CHCHO = H₂O + Me₂CHCH₂OMe₂CHO (I). Hexahydrobenzaldehyde, because of its sensitivity, must be used in the form of its NaHSO₃ compound and an extra mol. of HCHO must be employed to combine with the NaHSO₃. With aldehydes having a CH₂ adjacent to the CHO group, the reaction may be more complicated and result in the formation of diamino or aminohydroxy aldehydes in addition to the amino aldehydes. Thus, iso-BUCHO with 1 mol. HCHO and amine each yields chiefly the amino aldehyde (II), but with 2 mols. HCHO is formed the compound Me₂CHCH₂CH₂OH (CH₂NH₂)CHO (III) which loses 1 mol. HCHO with great ease (treatment with NaHSO₃ in water suffices) to form II. EtCHO with 1 mol. each of HCHO and Me₂NH gives a mixture of MeCH(CH₂NH₂)CHO (IV) and MeC(CH₂NH₂)₂CHO (V) but with 2 mols. each of HCHO and amine forms only V; the yields, however, are poor, and a considerable quantity of the R₂NH.HCl remains unchanged. AcH, HCHO and Me₂NH.HCl react at room temperature with evolution of heat but it is very difficult to isolate homogeneous products. In 1 experiment only, with 3 mols. each of HCHO and Me₂NH.HCl, was there obtained a crystalline product (VI) which is so unstable in solution that it could not be recrystd. Analysis points to the composition C₈H₁₂O₃N₂C₁₂ and its structure is probably (HCl.R₂NCH₂)₂2C(CH₂OH)₂CHO.H₂O. On hydrolysis in water in the presence of dimethylhydrosorcinol (methone, dimesone) it splits off 1 mol. HCHO at room temperature and all 3 at the b. p., while Na-Hg in faintly acid solution gives the alc. (R₂NCH₂)₂2CHCH₂OH (VII). These amino aldehydes can be used for the preparation of the corresponding acids through the oxime and nitrile, and of the alc. bases, whose benzoates and p-aminobenzoates are of interest as possible anesthetics (cf. Diétrichs, C. A. 26, 1339). a, α-Dimethyl-β-dimethylaminopropionaldehyde (I), from iso-PrCHO, Me₂NH.HCl and paraaldehyde refluxed in absolute alc., b. 142-4°, HCl salt, hygroscopic, m. 152-3°; chloroaurate, m. 106°; oxime, m. 57° (HCl salt, m. 163°); semicarbazone, m. 160°; p-nitrophenylhydrazones-HCl, m. 174°; methiodide, m. 219-20°; cyanohydrin, oil which cannot be distilled without decomposition a, α-Dimethyl-β-dimethylaminopropyl alc., from I in AcOH with Na-Hg, b. 166-8°, HCl salt, m. 136°; methiodide, m. 222°; benzoate-HCl, m. 153°; p-nitrobenzoate, yellow, m. 35°; p-aminobenzoate, m. 79-80°. a, α-Dimethyl-β-dimethylaminopropionitrile, from the oxime of I and boiling Ac₂O, b. 172° (HCl salt, m. 145°); HCl salt of acid, m. 150-1°. a-Hydroxymethyl-α-N-piperidinomethylisovaleraldehyde (III), obtained in 70% yield as the HCl salt, m. around 145° (decomposition). a-(Dimethylaminomethyl)butyraldehyde (11.7 g. from 21 g. PrCHO), b. 19 60°; HCl salt, m. 105°. a-(Dimethylaminomethyl)propionaldehyde (IV), b. 15 45°. a, α-Bis(dimethylaminomethyl)propionaldehyde (V), b. 15 83°. β-Hydroxy-α, α-bis(dimethylaminomethyl)propionaldehyde-2HCl (VI), needles with 1 H₂O, m. around 105°. a-(Dimethylaminomethyl)-β-dimethylaminopropanol (VII), b. 11 95-102°; benzoate-HCl, m. 242°; p-nitrobenzoate-HCl, m. 223°; p-aminobenzoate-HCl, m. 230°. a, α-Dimethyl-β-diethylaminopropionaldehyde, b. 175-7° (semicarbazone, m. 124-5°); propyl alc., b. 12 90-1° (benzoate-HCl, m. 131-2°; p-nitrobenzoate-HCl, m. 160°;

L19 ANSWER 63 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN
 AB cf. C. A. 16, 2497. In view of the importance of plant syntheses, it is interesting to find that the simplest salts give, with CH₂O, the indicated N compds. under comparatively mild conditions. M. and L. have studied the reaction between sec. amines, CH₂O and aliphatic-aromatic ketones. The reaction is as follows: MeOC₆H₄COCH₂Me + CH₂O + HNC₅H₁₀.HCl = H₂O + MeOC₆H₄COCH₂CH₂NC₅H₁₀.HCl. The reaction in most cases proceeds easily and with good yields. It is carried out by boiling a mixture of the HCl salt of the amine with concentrated CH₂O solution and the ketone for 1 hr.; better still by warming the amine salt and the ketone with paraformaldehyde in alc. A large number of β-keto bases can be thus prepared, inasmuch as both the amine and the ketone may be varied widely. In exceptional cases the reaction does not proceed normally. The keto bases so obtained in the form of their solid HCl salts are relatively stable. Aqueous solns. on boiling decompose to give the amine and an unsatd. ketone. Superheated steam or dry distillation in vacuo produces the same effect. E. g., p-MeOC₆H₄COCH₂CH₂NCMe₂ gives NMe₂.HCl and MeOC₆H₄COCH₂CH₂, the latter in poor yield due to polymerization. The vinyl compound on reduction, yields propionanilone. Some of the free keto bases are solid; the liquid ones cannot be distilled in vacuo. The keto bases give normal oximes except in case of the NMe₂ derivs. The keto groups may be reduced by various well known methods. This synthesis of β-keto bases makes possible the synthesis of compds. of the type of adrenaline, tyramine, hordenine, etc., but with the N in the γ-position. The corresponding homolog of adrenaline caused no rise of blood pressure, but a fall. However, the C₆H₅ derivs. of the type PhCOCH₂CH₂NC₅H₁₀ are local anesthetics. Replacement of the Ph group by other groups also gave anesthetic compds. Reduction of the keto bases to the β-NH₂ alc. caused loss of anesthetic properties, but benzoylation caused marked anesthesia. The Et group and the N are here in the same positions as in cocaine. Some of these compds. produced are more anesthetic than cocaine, but are irritating. The p-H₂NC₆H₄COCH₂ esters of these 1,3-amino alc. are anesthetics. β-Piperidinoethyl phenyl ketone hydrochloride, obtained by boiling in absolute alc. C₅H₁₁N.HCl, paraformaldehyde and PhCO₂Me, leaflets from EtOH-Me₂CO, m. 192-3°, readily soluble in H₂O, MeOH, CHCl₃, difficultly in alc., Me₂CO, and EtOAc. Boiling in aqueous solution causes decomposition with formation of CH₂:CH₂CO₂Ph. The free base is a nondistillable oil. Picrate, needles from HOAc, m. 180.5°. Oxime, needles from dilute alc., m. 143°. 1,6-Dipiperidino-3,4-diphenylhexane-3,4-diol (α- and β-forms), prepared by placing a moist Et₂O solution of the above ketone in contact with activated Al and extracting with Et₂O in a Soxhlet, needles from CHCl₃, m. 230° with brown coloration. HCl salt, m. 270°. This is the α-form. The β-form, obtained from the mother liquors of the α-form by treatment with HCl, followed by alkali, plates from alc., m. 115°. Probably one of these forms is the di-, the other the meso-compound [β-Piperidinoethyl]phenylcarbinol, by reduction of the HCl salt of the corresponding ketone base in H₂O by H and palladiumized charcoal; HCl salt, crystals from CHCl₃-EtOAc, m. 139°. Treatment with NH₄OH gives an oil crystallizing from MeOH, in leaflets, m. 68-9°. Picrate, needles, m. 103°. The same is obtained by reduction with Zn dust and HI. Hydrochloride of benzoate, by the action of BzCl on the base in CHCl₃, flat needles, m. 170°, is strongly anesthetic. p-Nitrobenzoyl ester, by boiling the base in C₆H₅ with p-O₂NC₆H₄COCl, brown needles from alc., m. 104°. p-Aminobenzoate, from the NO₂ compound with Sn and HCl at 40°, needles from ether, m. 118°; solns. of the HCl salt are strongly anesthetic. β-

L19 ANSWER 62 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 p-aminobenzoate-HCl (larocaine), m. 196°. a, α-Dimethyl-β-piperidinopropionaldehyde, b. 12 95° (HCl salt, m. 164°; chloroaurate, m. 116°; chloroplatinate, m. 167°; oxime-HCl, m. 169°; semicarbazone, m. 175°; cyanohydrin methiodide, m. 211°); propyl alc., b. 39 140° (HCl salt, m. 204°; benzoate-HCl, m. 152°); p-nitrobenzoate-HCl, m. 162-3°; p-aminobenzoate-HCl, m. 218°). a-(Piperidinomethyl)hexahydrobenzaldehyde, b. 15 140-2° (HCl salt, m. 165° (decompn.)); nitrate, m. 164°; oxime-HCl, m. 178°; methiodide, m. 160°); benzyl alc., b. 15 155-7° (HCl salt, m. 181°); methiodide, m. 148°; benzoate-HCl, m. 177°; p-nitrobenzoate-HCl, m. 134°; p-aminobenzoate-HCl, m. 230°). a-(Dimethylaminomethyl)hexahydrobenzaldehyde, b. 17 102-4° (HCl salt, m. 130°); oxime-HCl, m. 179°; methiodide, m. 223°); benzyl alc., b. 20 127-9° (HCl salt, m. 144°; methiodide, m. 178°; benzoate-HCl, m. 145°; p-nitrobenzoate-HCl, m. 185°; p-aminobenzoate-HCl, m. 193°). a-(N-Piperidinomethyl)isovaleraldehyde, b. 18 119-20° (HCl salt, m. 142° (decompn.)); isoamyl alc., b. 17 134-6° (benzoate-HCl, m. 155°; p-nitrobenzoate-HCl, m. 189°; p-aminobenzoate-HCl, m. 222°). a-Hydroxymethyl-α-(dimethylaminomethyl)isovaleraldehyde, m. 149° (decompn.). a-(Dimethylaminomethyl)isovaleraldehyde, b. 13 63-6° (HCl salt, m. 120° (decompn.)); methiodide, m. 145°; oxime-HCl, m. 133°); isoamyl alc., b. 13 80° (benzoate-HCl, m. 180°; p-nitrobenzoate-HCl, m. 176°; p-aminobenzoate-HCl, m. 167°). a-(Dimethylaminomethyl)butanol, b. 14 70-1° (HCl salt, m. 81°; benzoate-HCl, m. 159°; p-nitrobenzoate-HCl, m. 163°; p-aminobenzoate-HCl, m. 163°). a-(Dimethylaminomethyl)propanol, b. 12 60-5° (benzoate-HCl, m. 142°; p-nitrobenzoate-HCl, m. 183°; p-aminobenzoate-HCl, m. 165°). a, α-Bis(dimethylaminomethyl)propanol, b. 100-2° (benzoate-HCl, m. 196°; p-nitrobenzoate-HCl, m. 209°).
 ACCESSION NUMBER: 1932:28310 CAPLUS
 DOCUMENT NUMBER: 26:28310
 ORIGINAL REFERENCE NO.: 26:2965g-1, 2966a-g
 TITLE: A synthesis of N-substituted α-amino aldehydes
 AUTHOR(S): Mannich, C.; Lesser, B.; Silten, F.
 SOURCE: Ber. (1932), 65B, 378-85
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

L19 ANSWER 63 OF 65 CAPLUS COPYRIGHT 2005 ACS ON STN (Continued)
 Tetrahydroisoquinoline-β-phenyl ketone hydrochloride, by boiling tetrahydroisoquinoline-HCl in abs. alc. with paraformaldehyde and PhCO₂Me, m. 188°. The free base is a viscous oil, crystg. in an ice mixt. N,N'-Bis-[β-benzoyl-ethyl]piperazine, prep. in a similar manner from piperazine; the HCl salt turns brown at 190° without melting; the free base, by treatment with NH₃, crystals from 70% alc., m. 141°. Picrate, needles from PhNO₂, decomp. above 190°. Dioxime, m. 245°. β-Dimethylaminoethyl p-methoxyphenyl ketone, prep. from acetone, paraformaldehyde, and Me₂NH.HCl, crystals, as the HCl salt, needles from alc. m. 181°. Picrate, needles, m. 145°. By heating the HCl salt under 20 mm. at 180°, it decomps. to Me₂NH.HCl and vinyl anisyl ketone, m. 19°, unstable in liquid form, undergoing polymerization; dibromide, by the action of Br in CHCl₃, prisms from ligroin, m. 71°. Alc. PhNH₂Me₂ boiled with the ketone gives crystals, m. 105°, probably of 1-phenyl-3-p-methoxyphenylpyrazoline. Et anisyl ketone, prep. by reduction of the vinyl ketone, is identical with Klages' product (Ber. 35, 2262(1902)). β-Dimethylaminoethyl p-hydroxyphenyl ketone, prep. from the corresponding MeO compd. by boiling with HI. Hydroiodide, light yellow leaflets from alc., m. 205°. Alkalies do not cause sepn. of the free base from its aq. solns. [β-Dimethylaminoethyl]-p-anisylcarbinol hydrochloride, by reduction of the keto base with H and Pd, needles from CHCl₃-EtOAc, m. 203-4°. Free base, b. 130 146-8°, m. 53°. Benzoate, from the carbinol and BzCl in CHCl₃ on addn. of EtOAc, the HCl salt, m. 174°, seps. It is a powerful anesthetic. β-Piperidino-ethyl p-anisyl ketone, from C₅H₁₁N.HCl, acetone, and paraformaldehyde; HCl salt, needles, m. 216°. The free base is an oil which solidifies in an ice mixt. Picrate, short needles, m. 165°. Oxime, needles from alc., m. 136°. N,N'-Bis-[β-p-anisoyl-ethyl]piperazine, from piperazine, HCl, acetone, and paraformaldehyde. The HCl salt becomes brown at 150° without melting. Free base, yellowish leaflets, m. 173°, turning brown at 171°. β-Piperidinoisopropyl p-anisyl ketone, prep. in a similar manner from Et p-anisyl ketone; HCl salt, leaflets from abs. EtOH-Me₂CO, m. 178°. The free base is an oil. Oxime, m. 99°. β-Dimethylaminoethyl 3,4-dimethoxyphenyl ketone, by heating acetoveratrons, Me₂NH.HCl, and paraformaldehyde in abs. alc., is a viscous oil. The HCl salt m. 181-2°; picrate, needles, m. 157°. β-Dimethylaminoethyl 3,4-dihydroxyphenyl ketone hydroiodide, from the above MeO compd. with HI, light yellow crystals, m. 196°. Alkalies give no ppt. I-[γ-Dimethylaminopropyl]-3,4-dimethoxybenzene hydrochloride, by reduction of the HCl salt of the corresponding keto base with H and Pd, needles from Me₂CO, m. 195°. Free base, colorless and odorless oil, b. 330 161-4°. β-Piperidinoethyl 3,4-dimethoxyphenyl ketone, prep. from C₅H₁₁N.HCl, acetoveratrons, and paraformaldehyde; HCl salt, prisms, m. 183°. Free base, m. 113°. Picrate, m. 180°. Oxime, needles from alc., m. 168°. N,N'-Bis-[β-veratroyl-ethyl]piperazine, prep. in a similar manner from piperazine; HCl salt, short needles from 10% HCl, decomp. at 150° with brown coloration. Free base, yellow needles, m. 168°. β-Dimethylaminoethyl veratroyl ketone hydrochloride, prep. from Et₂NH.HCl by the usual method, needles from EtOAc, m. 140-1°. The free base is a nondistillable oil. Picrate, m. 136°; oxime, m. 104°. 1-Piperidino-2,3-diphenyl-3-propanone, prep. from desoxybenzoin, C₅H₁₁NH.HCl, and paraformaldehyde, crystals from 90% alc., m. 91°. The HCl salt is hygroscopic, but the HNO₃ salt forms difficultly sol. needles, m. 117°. β-[α-Dimethylaminopropyl]tetralin, prep. from acetotetralin; HCl salt, needles from Me₂CO, m. 170°. The free base is an oil;

L19 ANSWER 63 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 AB picrate, needles, m. 156". O-Dimethylaminoethyl- β -ar-tetrahydronaphthylcarbinol, prepd. by reducing the HCl salt of the above keto base with 14 and Pd; HCl salt, leaflets from Me₂CO, m. 163". The free base is an oil. β -(α -Piperidinopropyl)-tetralin; HCl salt, needles from Me₂CO, m. 170", crystals from water with water of crystn. and m. 85". This free base is an oil. Nitrate, difficultly sol. in water, m. 134-5". Oxine HCl salt, silky needles from dil. alc., m. 211".

ACCESSION NUMBER: 1923:10265 CAPLUS
 DOCUMENT NUMBER: 17:10265
 ORIGINAL REFERENCE NO.: 17:1795b-1,1796a-1,1797a-b
 TITLE: Synthesis of β -keto bases from aliphatic-aromatic ketones, formaldehyde, and secondary amines

AUTHOR(S): Mannich, C.; Lammring, D.
 SOURCE: Ber. (1922), 55B, 3510-26
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 17:10265

L19 ANSWER 64 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB Chemical reactions in solid, liquid, and gaseous substances, which are liable to disturbance by exothermic heating, are effected by heating the finely divided substance or mixture of substances by passage through molten metal kept at a suitable temperature by the rapid distribution of any locally developed heat to the molten metal, undesired secondary reactions are avoided. Examples of reactions to which the invention may be applied are the destructive distillation of wood, the oxidation of CH₄ to HCHO, and, according to the provisional specification, the distillation of Ca acetate; thus, finely subdivided wood such as sawdust or shavings is fed to a bath of molten lead at 350° and caused to travel therethrough by a rotating drum or by means of a travelling endless band, as described in 174,974; a mixture of CH₄ and air or O is passed in the form of fine bubbles through molten metal heated to 350-400°, preferably in the still described in 170,617, (C. A. 16, 1119) the mixed gases being pumped into the hood and issuing therefrom as fine bubbles into the corrugations of the inclined plate.

ACCESSION NUMBER: 1922:13648 CAPLUS
 DOCUMENT NUMBER: 16:13648
 ORIGINAL REFERENCE NO.: 16:2376d-g
 TITLE: Effecting chemical reactions
 PATENT ASSIGNEE(S): Thermal Industrial & Chemical (T.I.C.) Research Co., Ltd.; Morgan, J. S.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 176438		19201102	GB	

L19 ANSWER 65 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN
 AB In the early days of the natural gas industry, there were frequent cases of trouble in the mains caused by condensation of certain hydrocarbons. This was eliminated by the installation of drips from which the condensate, called "drip gasoline," was periodically removed and refined. About this time Mr. George Seybolt conceived the idea that there might be enough of these heavier hydrocarbons to pay for extn., and designed an apparatus which has proved very successful for this purpose. Natural gas is composed almost entirely of paraffin hydrocarbons, the lighter ones of the series being practically fixed, but the heavier being condensed with moderately low temps. and increased pressures. This condensate, consisting largely of pentane and hexane, forms an exceptionally high-test motor fuel and may be mixed with low-test gasoline to form a much larger quantity of a quality which is still acceptable. Moreover, aside from motor fuel, there are many valuable uses for these products. A fraction distilling between 40 and 70°, and consisting essentially of pentane and hexane, is chlorinated in the presence of ultraviolet light, amyl chloride distilled from the mixture, and the product heated under pressure with sodium acetate to form amyl acetate and salt, the former being a valuable solvent. A great potential possibility lies in the production of fatty acids for foods from hexane, heptane and octane; further, by simple "cracking" operations benzene and toluene can be produced. Other products are propane and butane; they remain in the by-product vapors from the condenser after passing under pressure through an absorbent oil, and are condensed and separated by certain conditions of temperature and pressure. These gases, compressed in cylinders, are used for lighting isolated buildings and as fuel for stationary and automobile engines, a mixer being used in place of a carburetor. Tables show the power of performance to be much better than with gasoline. As a torch fuel for metal cutting and welding, butane has the advantages of a narrow explosive range and low liquifying pressure. Researches on the behavior of natural gas, vent tank gas, propane and butane, when subjected to heat in the presence of catalysts have shown that the products resulting were characteristic for each catalyst or each set of conditions. An industrial application occurs in the production of carbon black which, after yielding the product desired, gives a volume of gas 1.27 to 2.99 times larger than the original and still has a heating value much superior to that of any artificial gas. However, this discharge gas contains unsatd. hydrocarbons of the olefin series which may be removed and used if desired to produce glycols, industrial alcohol, acetaldehyde, acetic acid, acetone, chlorinated olefine solvents, and other derivatives. Under the heading "Reactions with Air or Oxygen" the author takes up a number of patents on the production of methyl alcohol, formaldehyde, formic acid, carbon dioxide, and secondary products such as phosgene and oxalic acid; and under "Reactions with Chlorine" he discusses carbon tetrachloride, chloroform, methylene chloride, and muriatic acid. He shows also how the exhaust gas of a gas engine can be separated by means of compression and absorption into H₂O, CO₂, N, and argon, which, in turn, are utilized in various chemical industries. Also in Gas Age 41, 555-60 (1918).

ACCESSION NUMBER: 1918:10678 CAPLUS
 DOCUMENT NUMBER: 12:10678
 ORIGINAL REFERENCE NO.: 12:1826c-1,1827a-b
 TITLE: Whole natural gas industry today responsive to problem of chemical possibilities of natural gas

AUTHOR(S): Garner, J. B.
 SOURCE: American Gas Engineering Journal (1918), 108, 489-95, 505-9
 CODEN: AGEJAN; ISSN: 0096-4387

L19 ANSWER 65 OF 65 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable

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FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005

L1 1 S FORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005

L2 61794 S 50-00-0/RN
L3 166261 S N-METHYL?
L4 1415128 S ?AMINE
L5 889 S L2 AND L3 AND L4
L6 362618 S DISTILL?
L7 47 S L5 AND L6
L8 135208 S FORMALDEHYDE
L9 53548 S L8 AND L2
L10 143454 S L8 OR L2
L11 3718 S L10 AND L3
L12 2315 S L11 AND L4
L13 2268 S L12 NOT L7
L14 36 S L13 AND L6
L15 411299 S SECONDARY
L16 1271 S L15 AND L9
L17 72 S L16 AND L6
L18 65 S L17 NOT L7
L19 65 S L18 NOT L14

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=> s paraformaldehyde/cn
L20          1 PARAFORMALDEHYDE/CN
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L20 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
 RN 30525-89-4 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN Paraformaldehyde (9CI) (CA INDEX NAME)
 OTHER NAMES:
 CH Aldacide
 CN Flo-Mor
 CN Paraform
 DR 53026-80-5
 MF (C H2 O)x
 CI PMS, COM
 PCT Polyether, Polyether formed
 LC STN Files: ADISNEWS, AGRICOLA, ANABSTR, AQUIRE, BIOBUSINESS, BIOSIS,
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L3 166261 S N-METHYL?
L4 1415128 S ?AMINE
L5 889 S L2 AND L3 AND L4
L6 362618 S DISTILL?
L7 47 S L5 AND L6
L8 135208 S FORMALDEHYDE
L9 53548 S L8 AND L2
L10 143454 S L8 OR L2
L11 3718 S L10 AND L3
L12 2315 S L11 AND L4
L13 2268 S L12 NOT L7
L14 36 S L13 AND L6
L15 411299 S SECONDARY
L16 1271 S L15 AND L9
L17 72 S L16 AND L6
L18 65 S L17 NOT L7

L19 65 S L18 NOT L14

FILE 'REGISTRY' ENTERED AT 17:18:49 ON 15 JUN 2005
L20 1 S PARAFORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 17:19:34 ON 15 JUN 2005

=> s paraformaldehyde/cn

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

L22 5424 L21

=> fil caplus

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FILE LAST UPDATED: 14 Jun 2005 (20050614/ED)

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=> s paraformaldehyde/cn

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...
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L24 5424 L23

=> s 30525-89-4/rn

5424 30525-89-4

452 30525-89-4D

L25 5027 30525-89-4/RN

(30525-89-4 (NOTL) 30525-89-4D)

=> s l24 or l25

L26 5424 L24 OR L25

=> d his

(FILE 'HOME' ENTERED AT 16:45:02 ON 15 JUN 2005)

FILE 'REGISTRY' ENTERED AT 16:45:41 ON 15 JUN 2005

L1 1 S FORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 16:46:19 ON 15 JUN 2005

L2 61794 S 50-00-0/RN

L3 166261 S N-METHYL?

L4 1415128 S ?AMINE

L5 889 S L2 AND L3 AND L4

L6 362618 S DISTILL?

L7 47 S L5 AND L6

L8 135208 S FORMALDEHYDE

L9 53548 S L8 AND L2

L10 143454 S L8 OR L2

L11 3718 S L10 AND L3

L12 2315 S L11 AND L4

L13 2268 S L12 NOT L7

L14 36 S L13 AND L6

L15 411299 S SECONDARY

L16 1271 S L15 AND L9

L17 72 S L16 AND L6

L18 65 S L17 NOT L7

L19 65 S L18 NOT L14

FILE 'REGISTRY' ENTERED AT 17:18:49 ON 15 JUN 2005

L20 1 S PARAFORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 17:19:34 ON 15 JUN 2005

S PARAFORMALDEHYDE/CN

FILE 'REGISTRY' ENTERED AT 17:19:47 ON 15 JUN 2005

L21 1 S PARAFORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 17:19:47 ON 15 JUN 2005

L22 5424 S L21

FILE 'CAPLUS' ENTERED AT 17:19:54 ON 15 JUN 2005

S PARAFORMALDEHYDE/CN

FILE 'REGISTRY' ENTERED AT 17:20:06 ON 15 JUN 2005

L23 1 S PARAFORMALDEHYDE/CN

FILE 'CAPLUS' ENTERED AT 17:20:07 ON 15 JUN 2005

L24 5424 S L23
L25 5027 S 30525-89-4/RN
L26 5424 S L24 OR L25

=> s 126 and 13
L27 344 L26 AND L3

=> s 127 and 14
L28 212 L27 AND L4

=> s 128 and 16
L29 9 L28 AND L6

=> d 129 1-9 abs ibib

L29 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB In a process for production of an aromatic azomethine by reaction of an aniline with formaldehyde, formaldehyde is provided in the form of a product produced by contacting paraformaldehyde with from about 0.25 to about 3 mol equivalent of an aliphatic alc. having from 1 to 4 carbon atoms in the presence of a catalytic amount of a base. The azomethine may then be used to produce a haloacetanilide. Thus, e.g., one reactor was charged with 3.0 mol paraformaldehyde, 3.0 mol ethanol, 0.01 mol triethylamine, 1.0 mol xylene and 0.5 mol water, heated to 85-90° and agitated until the solution was clear; this solution was added to a reactor containing 1 mol of 2-methyl-6-ethylaniline and 2 mol of xylene at about 90°; the reaction was allowed to proceed with azeotropic distillation of water at atmospheric pressure at 95-126°; addition of chloroacetyl chloride afforded 96-97% of the N-chloromethyl-a-chloroacetanilide derivative

ACCESSION NUMBER: 1995:603984 CAPLUS
DOCUMENT NUMBER: 123:111656
TITLE: Process for producing aromatic azomethines by reaction of an aniline with formaldehyde provided in the form of a formaldehyde-alcohol complex
INVENTOR(S): Rodriguez, Gilbert
PATENT ASSIGNEE(S): Imperial Chemical Industries PLC, UK
SOURCE: U.S., 7 pp. Cont.-in-part of U.S. Ser. No. 680,468, abandoned.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5399759	A	19950321	US 1992-872775	19920422
HU 65592	A2	19940728	HU 1993-2620	19920320
HU 219568	B	20010528		
AT 154000	E	19970615	AT 1992-910655	19920320
ES 2102503	T3	19970801	ES 1992-910655	19920320
ZA 9202455	A	19930329	ZA 1992-2455	19920403
IL 101484	A1	19970415	IL 1992-101484	19920403
PRIORITY APPLN. INFO.:			US 1991-680468	B2 19910404
OTHER SOURCE(S):			CASREACT 123:111656; MARPAT 123:111656	

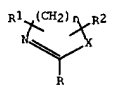
L29 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB The hazardous materials regulations under the Federal Hazardous Materials Transportation Act are revised based on the United Nations recommendations on the transport of dangerous goods. The regulations cover the classification of materials, packaging requirements, and package marking, labeling, and shipping documentation, as well as transportation modes and handling, and incident reporting. Performance-oriented stds. are adopted for packaging for bulk and nonbulk transportation, and SI units of measurement generally replace US customary units. Hazardous material descriptions and proper shipping names are tabulated together with hazard class, identification nos., packing group, label required, special provisions, packaging authorizations, quantity limitations, and vessel stowage requirements.

ACCESSION NUMBER: 1992:135528 CAPLUS
DOCUMENT NUMBER: 116:135528
TITLE: Performance-oriented packaging standards; changes to classification, hazard communication, packaging and handling requirements based on UN standards and agency initiative
CORPORATE SOURCE: United States Dept. of Transportation, Washington, DC, 20590-0001, USA
SOURCE: Federal Register (1990), 55(246), 52402-729, 21 Dec 1990
CODEN: FEREC; ISSN: 0097-6326
DOCUMENT TYPE: Journal
LANGUAGE: English

L29 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

GI



AB Oxazoline and imidazoline derivs. [I; R = C1-19 hydrocarbon, alkoxyalkyl, haloalkyl, trifluoromethyl, alkoxy, amino, alkylamino; R1, R2 = H, alkyl, trifluoromethyl, alkoxyalkyl, alkoxyalkyl, alkyl, and acrylaminoalkyl, etc.; X = O, NR3 (R3 = H, alkyl, alkenyl, alkoxyalkyl, carbalkoxyalkyl etc.); n = 2-3] are prepared as penetration enhancers. 2-(2-Aminoethylamino)ethanol and Et dodecanoate were heated before Et was replaced with toluene and refluxed to remove water than distilled to give 1-(2-hydroxyethyl)-2-undecyl-2-imidazoline (II). A cream formulation containing isosorbide dinitrate 0.7 and II 2% was applied on the human stratum corneum and then it was put between diffusion cells. The average cumulative amount of II in the receptor side of diffusion cell after 48 h was 872 µg as compared to 535 for control with no II. Several topical formulation of therapeutic agents with above penetration enhancers are given.

ACCESSION NUMBER: 1991:663486 CAPLUS
DOCUMENT NUMBER: 115:263486
TITLE: Preparation of oxazoline and imidazoline derivatives as body-membrane penetration enhancers
INVENTOR(S): Rajadhyaksha, Vithal J.
PATENT ASSIGNEE(S): USA
SOURCE: U.S., 17 pp. Cont.-in-part of U.S. 4,876,249.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5030629	A	19910709	US 1989-393584	19890811
US 4876249	A	19891024	US 1987-2387	19870112
PRIORITY APPLN. INFO.:			US 1987-2387	A2 19870112
OTHER SOURCE(S):			US 1989-345457	B2 19890501
			MARPAT 115:263486	

L29 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN

AB RNHC2P(O)(OH)2 (I; R = alkyl, aralkyl cycloalkyl), useful as dye intermediates, herbicides (no data), and fire retardants on cellulosic materials, were prepared MeNHAc, AcOH, Ac2O, and paraformaldehyde were heated at 116° for 30 min and the mixture was cooled to 25°. PC13 was added, and the mixture was kept at 59-70° for 45 min followed by heating to 130° over 3 h. The mixture was cooled to 100° and H2O was added, followed by distillation of H2O/HOAc. Aqueous H2SO4 was added and the mixture was refluxed 6 h. MeOH was added to precipitate I (R = Me).

ACCESSION NUMBER: 1989:595080 CAPLUS
DOCUMENT NUMBER: 111:195080
TITLE: Process for preparation of substituted-aminomethylphosphonic acids as herbicides, fire retardants, and dye intermediates
INVENTOR(S): Feeman, James F.
PATENT ASSIGNEE(S): Crompton and Knowles Corp., USA
SOURCE: U.S., 6 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4830788	A	19890516	US 1987-123222	19871120
CA 1338739	A1	19961126	CA 1989-591143	19890215
JP 02221288	A2	19900904	JP 1989-40456	19890222
JP 05043713	B4	19930702		
EP 385014	A1	19900905	EP 1989-302181	19890303
PRIORITY APPLN. INFO.:			DE, ES, FR, GB, GR, IT, LI, LU, NL, SE	19871120
OTHER SOURCE(S):			CASREACT 111:195080; MARPAT 111:195080	

L29 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2005 ACS ON STN

AB The title compds. H2C:CR1CONHCH2OR2 (R1 = H, Me; R2 = Bu, CH2CHMe2, CHMeEt, CHMe3), useful as crosslinking monomers for coatings, are manufactured by hydroxymethylating H2C:CR1CONH2 with HCHO in R2OH in the presence of an alkaline catalyst, etherifying the resulting H2C:CR1CONHCH2OR with addnl.

R2OH in the presence of an acid catalyst, and distilling off the solvent at pH 2-5. Thus, 71.7 g acrylamide was treated with 56.3 g paraformaldehyde in 37.1 g BuOH at pH 10.0 (by Et3N) at 50° to give N-methylolacrylamide (I), which was treated with addnl. 425.2 g BuOH under reflux at pH 3.0 (by oxalic acid). The reaction mixture was readjusted at pH 3.0 by oxalic acid and concentrated under reduced pressure

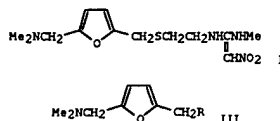
at 90° to give 163.2 g product containing N-butoxymethylacrylamide 98.2, 1 0.3, and acrylamide 1.5%.

ACCESSION NUMBER: 1988:205254 CAPLUS
DOCUMENT NUMBER: 108:205254
TITLE: Method of making N-alkoxymethyl(meth)acrylamides
INVENTOR(S): Watanabe, Seiichi; Sakasai, Kazuya; Tanaka, Yoshinori
PATENT ASSIGNEE(S): Mitsui Toatsu Chemicals, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 5
CODEN: JOKXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63005068	A2	19880111	JP 1986-146828	19860625
JP 07033362	B4	19950412	JP 1986-146828	19860625

PRIORITY APPLN. INFO.:
OTHER SOURCE(S): CASREACT 108:205254; MARPAT 108:205254

L29 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2005 ACS ON STN
GI



AB The title compound (I) [i.e. ranitidine] is prepared from furfuryl alc. (II) via the intermediate (dimethylaminomethyl)furanymethyl derivs. III (R = OH) and III (R = Br). Condensation of II with paraformaldehyde and Me₂NH.HCl in Me₂CHOH at reflux, followed by evaporation, extraction, and distillation in vacuo, gave 62% III (R = OH). A solution of the latter in refluxing dichloroethane was treated dropwise with SOBr₂ in dichloroethane, followed by 8 h reflux, evaporation, and distillation in vacuo, to give 78% III (R = Br). The bromide was added dropwise over 4-5 h to a solution of HSC₂H₄NH₂ (1:CH₂NO₂)NMe₂ and KOH in Me₂CHOH at -2°, and the mixture was stirred for 20 h at room temperature, filtered, saturated with

HCl(g), and set aside to precipitate crystalline I.HCl.

ACCESSION NUMBER: 1988:150297 CAPLUS
DOCUMENT NUMBER: 108:150297
TITLE: Process for the preparation of the antiulcer agent N-2-[[[5-[(dimethylamino)methyl]-2-furanyl]methyl]thio]ethyl-N'-methyl-2-nitro-1,1'-ethenediamine
INVENTOR(S): Linan Castellet, Isidro
PATENT ASSIGNEE(S): Farmhispania S. A., Spain
SOURCE: Span., 7 pp.
CODEN: SFXOAX
DOCUMENT TYPE: Patent
LANGUAGE: Spanish
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ES 556593	A1	19870716	ES 1986-556593	19860625

PRIORITY APPLN. INFO.:
ES 1986-556593 19860625

L29 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2005 ACS ON STN

AB The title compds., HCONR1CH2NHCOCR2:CHMe3 (R1 = H or Cl-5 alkyl, and R2, R3 = H or Me) are prepared for copolymn. with unsatd. olefinic monomers to give self-crosslinking thermosetting copolymers. Thus, HCONH2 450 and paraformaldehyde 300 g are stirred at 110° for 1 hr to give N-methylolformamide, cooled to 40°, and 2 l. cyclohexane, 30g. hydroquinone Me ether, 710 g acrylamide, and 75 ml concentrated HCl are added; water is azeotropically distilled to give 97% yield of N-formyl-N'-acryloylmethylenediamine. A 20:336:20 (weight) acrylonitrile-butyl acrylate-N-acryloyl-N'-formylmethylenediamine polymer is prepared at 46-50° as a 38.7% aqueous dispersion (pH 2.4). Drying the dispersion at 95° gives a crosslinked, flexible, and insol. film.

ACCESSION NUMBER: 1975:459739 CAPLUS
DOCUMENT NUMBER: 83:59739
TITLE: Methylenediamine derivatives
INVENTOR(S): Ribka, Joachim; Plesch, Steffen; Engelhardt, Friedrich
PATENT ASSIGNEE(S): Cassella Farbwerke Mainkur A.-G.
SOURCE: Ger. Offen., 17 pp.
CODEN: GWXKX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2251921	A1	19740425	DE 1972-2251921	19721023
NL 7314178	A	19740425	NL 1973-14178	19731015
CA 997371	A1	19760921	CA 1973-183604	19731017
DD 109616	C	19741112	DD 1973-174175	19731019
FR 2203807	A1	19740517	FR 1973-37556	19731022
JP 49075522	A2	19740720	JP 1973-118012	19731022
AU 7361640	A1	19750424	AU 1973-61640	19731022
AT 7308922	A	19750915	AT 1973-8922	19731022
AT 330142	B	19760610		
GB 1412893	A	19751105	GB 1973-49023	19731022
SU 503505	D	19760215	SU 1973-1966744	19731022
IT 998840	A	19760220	IT 1973-30409	19731022
ES 419839	A1	19760401	ES 1973-419839	19731022
CH 589612	A	19770715	CH 1973-14866	19731022
BE 806399	A1	19740423	BE 1973-136964	19731023
US 3912780	A	19751014	US 1973-408486	19731023
CS 172877	P	19770128	CS 1973-7278	19731023

PRIORITY APPLN. INFO.:
DE 1972-2251921 A 19721023

L29 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2005 ACS ON STN

AB Foam-in-place polyurethanes of improved temperature and moisture resistance are prepared by treating a polyisocyanate with a polyhydroxy compound, obtained by

condensation of an aldehyde with a polyalc. which does not form cyclic acetals with HCHO. Thus, a mixture of 1,4-butanediol 900, (4-HOCH₂CH₂OC₆H₄)₂CHMe 316, paraformaldehyde 330 g., and 800 cc. C₆H₆ was refluxed, 3 g. p-toluenesulfonic acid added, the C₆H₆-H₂O azeotrope distilled, and the residual C₆H₆ removed by vacuum distillation to give the polyacetal (I) (OH number 65). Then, 87 g. MeC₆H₃(NCO)₂ (II) was

added dropwise with stirring to a mixture of 1 kg. I, 20 g. N-methyl-diethanolamine, and 20 g. triethanolamine at 90-100°. The mixture was heated an addnl. 0.5 hr. to give a resinous product (III) with a OH number of 54. III (200 g.), 4 g. of a mixture of oleic acid and diethylbis(hydroxyethyl)ammonium ion (not further defined), 4 g. water, and 60 g. II were mixed until foaming began to give a soft, cellular polyurethane, bulk d. 0.086 g./cc., elasticity 30%, tensile strength 1.62 kg./sq. cm., elongation 123%, resistance to further tearing 0.74 kg./cm., and compression hardness at 40% compression 156 kg./sq. cm.

ACCESSION NUMBER: 1959:20554 CAPLUS
DOCUMENT NUMBER: 53:20554
ORIGINAL REFERENCE NO.: 53:3771b-d
TITLE: High-molecular-weight polyurethan plastics
PATENT ASSIGNEE(S): Farbenfabriken Bayer Akt.-Ges.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 798209		19580716	GB	
US 2961428		1960	US	

L29 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN
 AB EtOH (90 cc.) containing 0.5 g. Na and 75 g. CF₂:CF₂ (I) shaken under N in a bomb 8 h. at 50° and the mixture distilled through a precision column give 101.7 g. HCF₂-CF₂OEt, b. 57.5°, n_D25 1.294, d₄25 1.1978. I and (CH₂OH)₂ treated in the same way give 98 (HCF₂CF₂OCH₂)₂, b₁₀₀ 86°, n_D25 1.3202, d₄25 1.4726, and 154 HCF₂CF₂OCH₂-CH₂OH, b₁₀₀ 94°, n_D25 1.3419, d₄25 1.4159. In a similar way the following HCF₂CF₂OEt are prepared: R = Cl₂H₂, 99% yield, b₄ 105°, n_D25 1.3968, d₄25 0.9831; Cl₂H₃, 80%, b₆ 170°, m. 20-3°, n_D25 1.4144, d₄25 0.9530; C₆H₁₁ 99%, b₁₀₀ 86°, n_D25 1.3848, d₄25 1.1526. When 100 g. Na₂CO₃ in 200 cc. H₂O buffered with Na₂HPO₄ or borax to pH 6-7 is shaken 9 h. in a N atmospheric in a Ag-lined bomb with so much I that the pressure at 120° is 350 lb., with readjustment of the pressure to 350 lb. whenever it has dropped to about 325 lb., 17 g. NaF is formed. The filtrate is evaporated to dryness, the residue extracted with EtOH, and the filtered EtOH extract evaporated on a steam bath, giving 177 g. salts (II), m. 175°. II (165 g.) treated with 135 cc. 35% H₂SO₄, the Na₂SO₄ filtered off, the filtrate extracted with ether, and the residue of the dried ether extract distilled, gives 75 g. HCF₂CF₂SO₃H.H₂O (III), b₅ 112-14.5°, m. 54°. III is very hygroscopic. Warming 40 g. III 1 h. with 35 cc. 50% EtOH under a reflux condenser and distilling the product give 100% HCF₂CF₂SO₃H (IV), b_{3.5} 90-2°. The following HCF₂CF₂SO₃NH₃R salts are prepared: R = H, m. 198° (Maquenne block); Me, m. 119-20.5°; Cl₂H₂, m. 155°; Ph, m. 235°, also formed when III is treated with PhNCO; 1-C₁₀H₇, m. 225°, also obtained from III and 1-C₁₀H₇NCO. Anhydrous III (81 g.) with 100 g. PCl₅ gives HCF₂CF₂SO₂Cl, b. 92-2.5°. I with NHRR' gives the following HCF₂-CONRR' (R, R' given): H, Bu, 90% yield, b₃₀ 113°, n_D25 1.4112, d₄25 1.1029; Bu, Bu, 62%, b₁₀ 107°, n_D25 1.4270, d₄25 1.0150; H, Ph, 71%, b₅ 114°, m. 58°; Me, Ph, 51% b₄ 104°, n_D25 1.5036, d₄25 1.2305. I (75 g.) and 50 g. NH₃ in 100 cc. ether containing 0.1 g. Cu(OAc)₂ under anhydrous conditions give, in an exothermic reaction, 82% 2,4,6-tris(diethylaminoethyl)-s-triazine (V), b₉ 73°, m. 24.5°, n_D25 1.3999, d₄25 1.5973. V does not react with Br in CCl₄, with dilute KMnO₄, or dilute HNO₂. Refluxing 22 g. V with 70 cc. 4 N NaOH 4 h., acidifying the aqueous filtrate with 30 cc. 50% H₂SO₄, and extracting it with ether give 22% HCF₂CO₂H, b. 131°. When 50 g. V is refluxed 50 h. with 75 cc. H₂O 7 g. V is recovered; the aqueous solution on evaporation gives 50 g. HCF₂CO₂NH₄. Heating 15 g. paraformaldehyde, 150 cc. concentrated H₂SO₄, and 50 g. I in a Ag-lined vessel 15 h. at 80°, pouring the mixture on ice, extracting the filtered solution with ether and the washed ether solution with 180 cc. H₂O containing 20 g. NaOH, and the acidified (36 cc. 50% H₂SO₄) solution again with ether give 16 g. oil, containing 80% HOCH₂CF₂CO₂H (VI), turns dark and becomes more viscous when heated at 250°/8 mm. Refluxed 11 h. with 23 g. EtOH and 60 g. CuSO₄, VI gives 7.9 g. HOCH₂-CF₂CO₂Et (VII), b₆ 58-61°, b₇₆₀ 181°, n_D25 1.3830. Hydrolysis of VII gives VI, m. 49-53°. Treating I at 300/70 lb. and 60° 15 h. with 100 g. iodine in 150 cc. ether gives 74% (CF₂I)₂, b₁₄ 23°, b₁₁₀ 51°, b. 112-13°, n_D25 1.4895, d₄25 2.6293, MR 40.3. N₂O₄ (57 g.) with I 8 h. at 7 lb. pressure gives 7.5% [CF₂(NO₂)₂]₂, b. 58-9°, d₄25 1.6024, n_D25 1.3265, MR 24.2.
 ACCESSION NUMBER: 1950:29898 CAPLUS

L29 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2005 ACS on STN (Continued)
 DOCUMENT NUMBER: 44:29898
 ORIGINAL REFERENCE NO.: 44:5796f-i,5797a-e
 TITLE: Addition reactions of tetrafluoroethylene
 AUTHOR(S): Coffman, D. D.; Raasch, M. S.; Rigby, G. W.; Barrick, P. L.; Hanford, W. E.
 CORPORATE SOURCE: E. I. du Pont de Nemours & Co., Wilmington, DE
 SOURCE: Journal of Organic Chemistry (1949), 14, 747-53
 CODEN: JOCEAH; ISSN: 0022-3263
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 44:29898

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COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

29.43

486.41

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

-6.57

-114.61

STN INTERNATIONAL LOGOFF AT 17:22:32 ON 15 JUN 2005